

# Supporting Information

## Oxidative Condensations to Form Benzimidazole-Substituted Potassium Organotrifluoroborates

*Gary A. Molander\* and Kehinde Ajayi*

Roy and Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania,  
Philadelphia, Pennsylvania 19104-6323

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**General Considerations.** All solvents were HPLC grade and were used as received.  $\text{NEt}_3$  was distilled from  $\text{CaH}_2$  prior to use. All catalysts, ligands, and other reagents were obtained commercially and used without further purification. Melting points ( $^\circ\text{C}$ ) were determined using a Thomas-Hoover melting point apparatus and are uncorrected.  $^{19}\text{F}$  NMR chemical shifts were referenced to external  $\text{CFCl}_3$  (0.0 ppm).  $^{11}\text{B}$  NMR spectra were obtained on a spectrometer equipped with the appropriate decoupling accessories. All  $^{11}\text{B}$  NMR chemical shifts were referenced to external  $\text{BF}_3\cdot\text{OEt}_2$  (0.0 ppm) with a negative sign indicating an upfield shift. Analytical thin layer chromatography (TLC) was performed on silica gel (60F-254) plates (0.25 mm) precoated with a fluorescent indicator, and preparative plate purifications were performed on silica gel plates (500  $\mu\text{m}$ ) precoated with a fluorescent indicator. Standard flash chromatography procedures were followed using 40-63  $\mu\text{m}$  silica gel. Visualization was effected with ultraviolet light or iodine on silica. High-resolution mass spectra were measured under electrospray ionization (ESI).

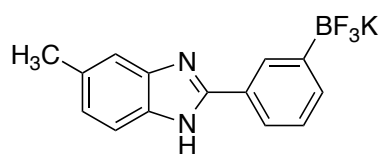
## **Synthesis of Benzimidazole-Substituted Potassium Organotrifluoroborates**

### **General Procedure A - Condensation of Potassium Formyl**

#### **Aryltrifluoroborates with 3,4-Toluenediamine**

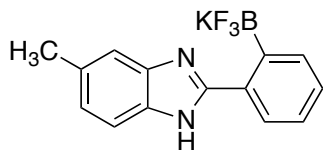
A microwave vial was charged with 69 mg (0.55 mmol) of 3,4-diaminotoluene and dissolved in 2.8 mL of a 1:1 EtOH/MeCN mixture. To this solution was added 10  $\mu\text{L}$  (0.05 mmol) of a saturated aqueous  $\text{KHF}_2$  solution. The reaction mixture was purged

with O<sub>2</sub> for 20 seconds before allowing the reaction to stir for 2 min under positive oxygen pressure. The oxygenated reaction mixture was then charged with 0.5 mmol of the required trifluoroborate. The reaction was allowed to stir for the indicated time, at the indicated temperature, until judged complete by <sup>1</sup>H NMR. The reaction was concentrated, dissolved in 2 mL of acetone, and the product was precipitated with 10 mL of Et<sub>2</sub>O. The reaction was filtered, and the precipitate was washed with 15 mL Et<sub>2</sub>O and dried under vacuum to yield pure benzimidazole.



**Potassium (3-(5-Methyl-1H-benzo[d]imidazol-2-**

**yl)phenyl)trifluoroborate (2b).** Following general procedure A, potassium (3-formyl)phenyltrifluoroborate<sup>1</sup> (106 mg) was allowed to react for 10 h at 40 °C to give 173 mg of the title compound (92% yield) as a brown powder: mp >260 °C; <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 12.62 (br s, 1 H), 8.30 (s, 1 H), 7.99 (dd, *J* = 8.0, 1.0 Hz, 1 H), 7.62 (d, *J* = 7.5 Hz, 1 H), 7.40 (d, *J* = 8.0 Hz, 1 H), 7.34 (d, *J* = 0.5 Hz, 1 H), 7.26 (t, *J* = 2.5 Hz, 1 H), 6.98 (dd, *J* = 8.0, 1.0 Hz, 1 H), 2.40 (s, 3 H); <sup>13</sup>C NMR (125 MHz, acetone-*d*<sub>6</sub>) δ 153.9, 134.2, 132.0, 130.5, 129.3, 127.7, 124.9, 124.0, 118.4, 117.7, 115.8, 115.1, 114.3, 21.7; <sup>19</sup>F NMR (470 MHz, acetone-*d*<sub>6</sub>) δ -142.4; <sup>11</sup>B NMR (128 MHz, acetone-*d*<sub>6</sub>) δ 4.2; FTIR (neat) ν 2352, 1632, 1444, 1269, 1212, 957, 902, 799; HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>11</sub>N<sub>2</sub>BF<sub>3</sub> (M – K)<sup>–</sup> 275.0967, found 275.0965.



**Potassium (2-(5-Methyl-1H-benzo[d]imidazol-2-**

**yl)phenyl)trifluoroborate (2c).** Following general procedure A, potassium (2-

formyl)phenyltrifluoroborate<sup>1</sup> (106 mg) was allowed to react for 10 h at 40 °C to give

99.7 mg of the title compound (63% yield) as a tan powder: mp 250–252 °C (decomp);

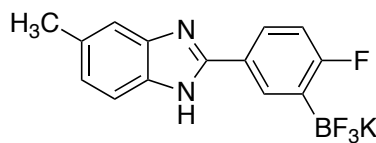
<sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 8.27–8.30 (m, 1 H), 7.85–7.87 (m, 1 H), 7.57 (d, *J* = 8.5 Hz, 1 H), 7.48–7.50 (m, 1 H), 7.40 (t, *J* = 3.5 Hz, 1 H), 7.38–7.41 (m, 1 H), 7.13 (dd, *J*

= 8.0, 1.0 Hz, 1 H), 2.56 (s, 3 H); <sup>13</sup>C NMR (125 MHz, acetone-*d*<sub>6</sub>) δ 156.2, 134.1, 131.4,

129.8, 128.4, 126.7, 123.5, 115.4, 115.0, 21.7; <sup>19</sup>F NMR (470 MHz, acetone-*d*<sub>6</sub>) δ -137.2;

<sup>11</sup>B NMR (128 MHz, acetone-*d*<sub>6</sub>) δ 4.2; FTIR (neat) ν 2919, 1616, 1456, 1190, 1141, 949,

801, 748; HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>11</sub>N<sub>2</sub>BF<sub>3</sub> (M – K)<sup>–</sup> 275.0967, found 275.0969.



**Potassium (2-Fluoro-5-(5-methyl-1H-**

**benzo[d]imidazol-2-yl)phenyl)trifluoroborate (2d).** Following general

procedure A, potassium (2-fluoro-5-formyl)phenyltrifluoroborate<sup>2</sup> (115 mg) was allowed

to react for 12 h at 40 °C to give 118 mg of the title compound (71% yield) as a purple-

brown powder: mp 215–218 °C (decomp); <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 8.26 (dd, *J*

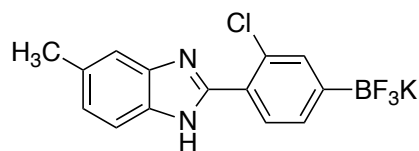
= 5.5, 2.0 Hz, 1 H), 8.01 (ddd, *J* = 8.5, 5.5, 2.5 Hz, 1 H), 7.44 (d, *J* = 8.5 Hz, 1 H), 7.36 (s,

1 H), 6.99 (d, *J* = 8.0 Hz, 1 H), 6.94 (t, *J* = 8.5 Hz, 1 H), 2.42 (s, 3 H); <sup>13</sup>C NMR (125

MHz, acetone-*d*<sub>6</sub>) δ 167.6 (d, *J* = 241 Hz), 153.0, 140.4, 139.3, 133.7 (d, *J* = 14 Hz), 132.1,

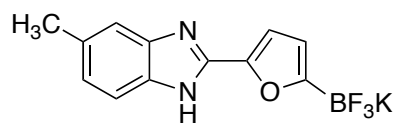
127.3, 126.0, 124.1, 115.7, 115.3, 115.1, 21.7; <sup>19</sup>F NMR (470 MHz, acetone-*d*<sub>6</sub>) δ 107.0 (m),

140.3;  $^{11}\text{B}$  NMR (128 MHz, acetone- $d_6$ )  $\delta$  3.3; FTIR (neat)  $\nu$  2920, 1632, 1454, 1280, 1183, 988, 960, 813; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{10}\text{N}_2\text{BF}_4$  ( $\text{M} - \text{K}$ ) $^-$  293.0873, found 293.0875.



**Potassium (3-Chloro-4-(5-methyl-1H-**

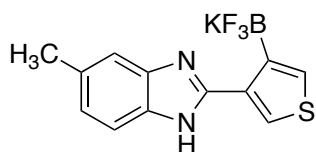
**benzo[*d*]imidazol-2-yl)phenyl)trifluoroborate (2e).** Following general procedure A, potassium (3-formyl)phenyltrifluoroborate<sup>2</sup> (123 mg) was allowed to react for 12 h at 40 °C to give 144 mg of the title compound (83% yield) as a light-brown powder: mp 228–235 °C (decomp);  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ )  $\delta$  7.90 (d,  $J$  = 7.5 Hz, 1 H), 7.61 (s, 1 H), 7.52 (d,  $J$  = 8.5 Hz, 1 H), 7.51 (d,  $J$  = 8.5 Hz, 1 H), 7.42 (s, 1 H), 7.04 (d,  $J$  = 8.0 Hz, 1 H), 2.43 (s, 3 H);  $^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ )  $\delta$  151.1, 139.8, 138.5, 134.2, 132.5, 131.4, 131.2, 131.0, 127.1, 124.4, 116.0, 115.4, 21.7;  $^{19}\text{F}$  NMR (470 MHz, acetone- $d_6$ )  $\delta$  -143.3;  $^{11}\text{B}$  NMR (128 MHz, acetone- $d_6$ )  $\delta$  3.5; FTIR (neat)  $\nu$  2863, 1629, 1544, 1445, 1409, 1211, 990, 839, 779; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{10}\text{N}_2\text{BClF}_3$  ( $\text{M} - \text{K}$ ) $^-$  309.0568, found 309.0578.



**Potassium (5-(5-Methyl-1H-benzo[*d*]imidazol-2-**

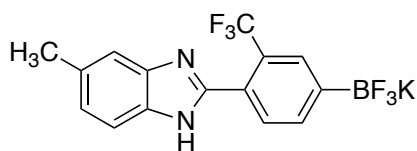
**yl)furan-2-yl)trifluoroborate (2f).** Following general procedure A, potassium (3-formyl)phenyltrifluoroborate<sup>3</sup> (101 mg) was allowed to react for 18 h at 40 °C to give 108 mg of the title compound (71% yield) as a burgundy powder: mp 120–123 °C (decomp);

$^1\text{H}$  NMR (500 MHz, acetone- $d_6$ )  $\delta$  11.73 (br s, 1 H), 7.41 (d,  $J$  = 8.0 Hz, 1 H), 7.33 (s, 1 H), 6.97 (dd,  $J$  = 8.5, 1.0 Hz, 1 H), 6.94 (d,  $J$  = 3.0 Hz, 1 H), 6.32 (d,  $J$  = 3.0 Hz, 1 H), 2.40 (s, 3 H);  $^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ )  $\delta$  146.3, 145.5, 132.2, 124.1, 113.7, 111.0, 21.6;  $^{19}\text{F}$  NMR (470 MHz, acetone- $d_6$ )  $\delta$  142.0;  $^{11}\text{B}$  NMR (128 MHz, acetone- $d_6$ )  $\delta$  1.6; FTIR (neat)  $\nu$  2932, 1610, 1443, 1206, 1175, 992, 894, 803; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{12}\text{H}_9\text{N}_2\text{OBF}_3$  ( $\text{M} - \text{K}$ ) $^-$  265.0760, found 265.0731.



**Potassium (4-(5-Methyl-1H-benzo[d]imidazol-2-**

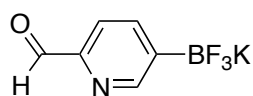
**yl)thiophen-3-yl)trifluoroborate (2g).** Following general procedure A, potassium (3-formyl)thienyltrifluoroborate<sup>4</sup> (109 mg) was allowed to react for 18 h at 40 °C to give 118 mg of the title compound (74% yield) as a brown powder: mp 185–190 °C (decomp);  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ )  $\delta$  8.11 (dd,  $J$  = 3.5, 1.0 Hz, 1 H), 7.41 (d,  $J$  = 8.5 Hz, 1 H), 7.34 (d,  $J$  = 3.5 Hz, 1 H), 7.32–7.33 (m, 1 H), 6.95 (dd,  $J$  = 8.0, 1.0 Hz, 1 H), 2.42 (s, 3 H);  $^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ )  $\delta$  151.7, 136.4, 131.7, 128.8, 126.7, 123.8, 115.2, 115.0, 21.7;  $^{19}\text{F}$  NMR (470 MHz, acetone- $d_6$ )  $\delta$  -136.7;  $^{11}\text{B}$  NMR (128 MHz, acetone- $d_6$ )  $\delta$  3.5 (q,  $J$  = 61 Hz); FTIR (neat)  $\nu$  2920, 1626, 1459, 1170, 1121, 947, 808, 718; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{12}\text{H}_9\text{N}_2\text{BF}_3\text{S}$  ( $\text{M} - \text{K}$ ) $^-$  281.0532, found 281.0681.



**Potassium (4-(5-Methyl-1H-benzo[d]imidazol-2-**

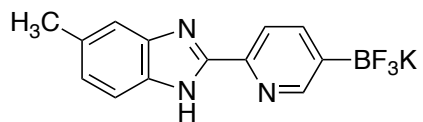
**yl)-3-(trifluoromethyl)phenyl)trifluoroborate (2h).** Following general

procedure A, potassium (4-formyl-3-trifluoromethyl)phenyltrifluoroborate<sup>4</sup> (140 mg) was allowed to react for 12 h at 40 °C to give 118 mg of the title compound (62% yield) as a brown powder: mp 251–253 °C (decomp); <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 7.99 (s, 1 H), 7.81 (d, *J* = 7.5 Hz, 1 H), 7.54 (d, *J* = 7.5 Hz, 1 H), 7.48 (d, *J* = 8.0 Hz, 1 H), 7.38–7.39 (m, 1 H), 7.08 (dd, *J* = 8.5, 1.0 Hz, 1 H), 2.45 (s, 3 H); <sup>13</sup>C NMR (125 MHz, acetone-*d*<sub>6</sub>) δ 151.6, 136.0, 132.4, 131.0, 130.1, 128.1, 127.2, 127.1, 127.0, 124.9, 124.3, 116.1, 115.4, 21.7; <sup>19</sup>F NMR (470 MHz, acetone-*d*<sub>6</sub>) δ -56.5, -140.2; <sup>11</sup>B NMR (128 MHz, acetone-*d*<sub>6</sub>) δ 3.5; FTIR (neat) ν 2946, 1611, 1560, 1445, 1307, 1205, 1174, 990, 801; HRMS (ESI) *m/z* calcd for C<sub>15</sub>H<sub>10</sub>N<sub>2</sub>BF<sub>6</sub> (M – K)<sup>–</sup> 343.0841, found 343.0826.



**Potassium (6-Formylpyridin-3-yl)trifluoroborate.** A round

bottom flask with stir bar was charged with formylpyridin-5-boronic acid pinacol ester (990 mg, 3.9 mmol), MeOH (1 mL), and saturated aqueous KHF<sub>2</sub> (1.3 mL). The solution was stirred at rt under N<sub>2</sub> and, after 1 h, concentrated under reduced pressure. The crude residue was dissolved in a minimum amount of acetone, and the product was precipitated with Et<sub>2</sub>O, filtered, and dried under vacuum to yield 615 mg of the title compound in 91% yield as a yellow solid: mp >260 °C; <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 9.95 (d, *J* = 0.5 Hz, 1 H), 8.83 (s, 1 H), 7.94 (d, *J* = 7.0 Hz, 1 H), 7.70 (d, *J* = 7.5 Hz, 1 H); <sup>13</sup>C NMR (125 MHz, acetone-*d*<sub>6</sub>) δ 195.1, 154.7, 151.9, 140.6, 120.6; <sup>19</sup>F NMR (470 MHz, acetone-*d*<sub>6</sub>) δ -143.5; <sup>11</sup>B NMR (128 MHz, acetone-*d*<sub>6</sub>) δ 2.1; FTIR (neat) ν 1196, 1454, 1497, 1560, 1599, 1685, 2872; HRMS (ESI) *m/z*: calcd for C<sub>6</sub>H<sub>4</sub>BF<sub>3</sub>NO [M – K]<sup>–</sup> 174.0338; found 174.0346.



**Potassium (6-(5-Methyl-1*H*-benzo[*d*]imidazol-2-**

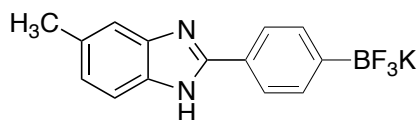
**yl)pyridin-3-yl)trifluoroborate (2i).** Following general procedure A, potassium (6-formylpyridin-3-yl)trifluoroborate (140 mg) was allowed to react for 12 h at 40 °C to give 118 mg of the title compound (62% yield) as a tan powder: mp >260 °C; <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 8.71 (s, 1 H), 8.16 (d, *J* = 7.5 Hz, 1 H), 7.94 (d, *J* = 7.5 Hz, 1 H), 7.52 (d, *J* = 8.0 Hz, 1 H), 7.44 (s, 1 H), 7.03 (d, *J* = 8.5 Hz, 1 H), 2.44 (s, 3 H); <sup>13</sup>C NMR (125 MHz, acetone-*d*<sub>6</sub>) δ 153.5, 153.1, 147.0, 140.8, 132.5, 124.4, 120.6, 21.7; <sup>19</sup>F NMR (470 MHz, acetone-*d*<sub>6</sub>) δ -142.8; <sup>11</sup>B NMR (128 MHz, acetone-*d*<sub>6</sub>) δ 3.8; FTIR (neat) ν 2918, 1596, 1438, 1221, 966, 849, 802; HRMS (ESI) *m/z* calcd for C<sub>13</sub>H<sub>10</sub>N<sub>3</sub>BF<sub>3</sub> (M – K)<sup>+</sup> 276.0920, found 276.0881.

### **General Procedure B. Condensation of Potassium 4-Formyl Phenyltrifluoroborate with Functionalized 1,2-Diaminoarenes**

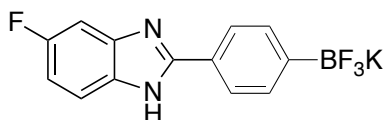
A microwave vial was charged with 0.55 mmol of the required substituted 1,2-diaminoarene and dissolved in 2.8 mL of a 2:1 EtOH/MeCN mixture. To this solution was added 10 μL (0.05 mmol) of a saturated aqueous KHF<sub>2</sub> solution. The reaction mixture was purged with O<sub>2</sub>, from a balloon, for 20 seconds before allowing the reaction to stir for 2 min. The oxygenated reaction mixture was then charged with 106 mg (0.5 mmol) of potassium 4-formyl phenyltrifluoroborate.<sup>1</sup> The reaction was allowed to stir



for the indicated time, at the indicated temperature, until judged complete by  $^1\text{H}$  NMR. The reaction was concentrated, dissolved in 2 mL of acetone, and the product was precipitated with 10 mL of  $\text{Et}_2\text{O}$ . The reaction was filtered, and the precipitate was washed with 15 mL  $\text{Et}_2\text{O}$  and dried under vacuum to yield pure benzimidazole.

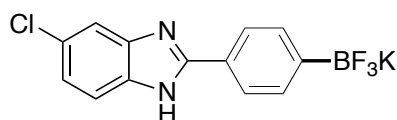


**Potassium (4-(5-Methyl-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (2a).** Following general procedure B, 3,4-diaminotoluene (69 mg) was allowed to react for 10 h at 40 °C to give 149 mg of the title compound (95% yield) as a tan powder: mp >260 °C;  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ )  $\delta$  7.99 (d,  $J$  = 8.0 Hz, 2 H), 7.62 (d,  $J$  = 7.5 Hz, 2 H), 7.45 (d,  $J$  = 8.0 Hz, 1 H), 7.36 (s, 1 H), 6.99 (d,  $J$  = 8.5 Hz, 1 H), 2.41 (s, 3 H);  $^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ )  $\delta$  153.8, 132.9, 132.1, 129.0, 128.4, 125.5, 124.0, 117.7, 116.6, 21.7;  $^{19}\text{F}$  NMR (470 MHz, acetone- $d_6$ )  $\delta$  -142.6;  $^{11}\text{B}$  NMR (128 MHz, acetone- $d_6$ )  $\delta$  3.1; FTIR (neat)  $\nu$  2919, 1634, 1418, 1220, 966, 834, 798; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{11}\text{N}_2\text{BF}_3$  ( $\text{M} - \text{K}$ ) $^-$  275.0967, found 275.0963.

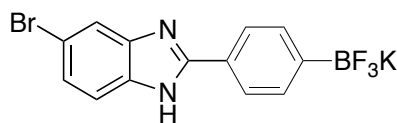


**Potassium (4-(5-Fluoro-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (2j).** Following general procedure B, 4-fluoro-1,2-diaminobenzene (71 mg) was allowed to react for 24 h at 40 °C to give 89.4 mg of the title compound (56% yield) as a tan powder: mp >260 °C;  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ )  $\delta$  11.84 (br s, 1 H), 7.96 (d,  $J$  = 7.5 Hz, 2 H), 7.64 (d,  $J$  = 8.0 Hz, 2 H), 7.43–7.60 (m, 1

H), 7.15–7.35 (m, 1 H), 6.95 (ddd,  $J = 10.0, 8.5, 2.5$  Hz, 1 H);  $^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ )  $\delta$  160.9, 155.5, 133.0, 129.1, 127.8, 125.4, 122.1, 116.7;  $^{19}\text{F}$  NMR (470 MHz, acetone- $d_6$ )  $\delta$  -116.1, -142.7;  $^{11}\text{B}$  NMR (128 MHz, acetone- $d_6$ )  $\delta$  3.9; FTIR (neat)  $\nu$  2911, 1624, 1415, 1216, 952, 834, 776; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_8\text{N}_2\text{BF}_4$  ( $\text{M} - \text{K}$ ) $^-$  279.0717, found 279.0734.

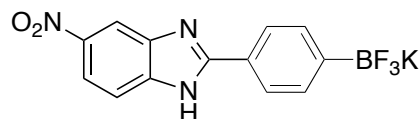


**Potassium (4-(5-Chloro-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (2k).** Following general procedure B, 4-chloro-1,2-diaminobenzene (81 mg) was allowed to react for 24 h at 40 °C to give 109 mg of the title compound (65% yield) as a brown powder: mp >260 °C;  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ )  $\delta$  12.15 (br s, 1 H), 8.01 (d,  $J = 7.5$  Hz, 2 H), 7.64 (d,  $J = 7.5$  Hz, 2 H), 7.58 (s, 1 H), 7.55 (d,  $J = 8.5$  Hz, 1 H), 7.16 (dd,  $J = 8.5, 1.5$  Hz, 1 H);  $^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ )  $\delta$  155.4, 133.0, 127.8, 127.5, 125.7, 122.8;  $^{19}\text{F}$  NMR (470 MHz, acetone- $d_6$ )  $\delta$  -142.7;  $^{11}\text{B}$  NMR (128 MHz, acetone- $d_6$ )  $\delta$  4.2; FTIR (neat)  $\nu$  2796, 1621, 1412, 1207, 957, 792, 781; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_8\text{N}_2\text{BClF}_3$  ( $\text{M} - \text{K}$ ) $^-$  295.0421, found 295.0409.

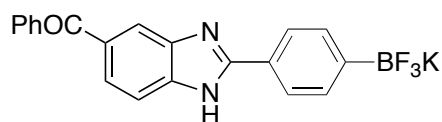


**Potassium (4-(5-Bromo-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (2l).** Following general procedure B, 4-bromo-1,2-diaminobenzene (105 mg) was allowed to react for 24 h at 40 °C to give 128 mg of the title compound (68% yield) as a purple-ish powder: mp >260 °C;  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ )  $\delta$  8.00 (d,  $J = 7.5$  Hz, 2 H), 7.74 (s, 1 H), 7.65 (d,  $J = 8.0$  Hz, 2 H), 7.51 (d,  $J$

= 7.5 Hz, 1 H), 7.29 (dd,  $J$  = 8.5, 2.0 Hz, 1 H);  $^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ )  $\delta$  155.2, 133.0, 129.3, 127.6, 125.7, 125.5, 116.6, 115.0;  $^{19}\text{F}$  NMR (470 MHz, acetone- $d_6$ )  $\delta$  -142.8;  $^{11}\text{B}$  NMR (128 MHz, acetone- $d_6$ )  $\delta$  2.9; FTIR (neat)  $\nu$  2930, 1616, 1410, 1216, 967, 916, 834, 800; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_8\text{N}_2\text{BBrF}_3$  ( $\text{M} - \text{K}$ ) $^-$  338.9916, found 338.9911.

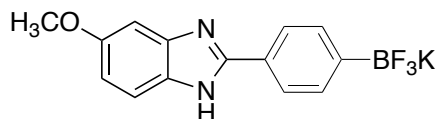


**Potassium (4-(5-Nitro-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (2m).** Following general procedure B, 4-nitro-1,2-diaminobenzene (84 mg) was allowed to react for 96 h at 60 °C to give 90.8 mg of the crude title compound (16% yield by  $^1\text{H}$  NMR) as a red powder:  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ )  $\delta$  8.04 (d,  $J$  = 8.0 Hz, 2 H), 7.85 (s, 1 H), 7.69 (d,  $J$  = 8.0 Hz, 2 H), 7.61 (d,  $J$  = 7.5 Hz, 1 H), 7.38 (dd,  $J$  = 8.0, 2.0 Hz, 1 H);  $^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ )  $\delta$  155.2, 134.5, 129.9, 126.9, 126.1, 125.7, 124.1;  $^{19}\text{F}$  NMR (470 MHz, acetone- $d_6$ )  $\delta$  -141.7;  $^{11}\text{B}$  NMR (128 MHz, acetone- $d_6$ )  $\delta$  3.8; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_8\text{N}_3\text{O}_2\text{BF}_3$  ( $\text{M} - \text{K}$ ) $^-$  306.0662, found 306.0717.



**Potassium (4-(5-Benzoyl-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (2n).** Following general procedure B, 3,4-diaminobenzophenone (120 mg) was allowed to react for 24 h at 40 °C to give 99.1 mg of the title compound (49% yield) as a yellow powder: mp >260 °C;  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ )  $\delta$  7.80 (d,  $J$  = 7.0 Hz, 2 H), 7.73 (d,  $J$  = 7.5 Hz, 2 H), 7.64–7.70 (m, 2 H), 7.63 (s, 1 H), 7.55–7.59 (m, 1 H), 7.52 (d,  $J$  = 8.0 Hz, 2 H), 7.49 (d,  $J$  = 8.5 Hz, 2 H);  $^{13}\text{C}$

NMR (125 MHz, acetone- $d_6$ )  $\delta$  194.7, 160.7, 150.3, 134.6, 133.0, 132.6, 131.9, 131.3, 130.4, 130.0, 129.1, 127.6, 126.6, 124.9;  $^{19}\text{F}$  NMR (470 MHz, acetone- $d_6$ )  $\delta$  -142.7;  $^{11}\text{B}$  NMR (128 MHz, acetone- $d_6$ )  $\delta$  3.8; FTIR (neat)  $\nu$  2930, 1674, 1616, 1430, 1216, 967, 916, 822; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{13}\text{N}_2\text{OBF}_3$  ( $\text{M} - \text{K}$ ) $^-$  365.1073, found 365.1099.

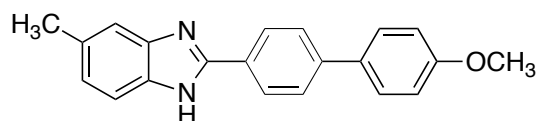


**Potassium (4-(5-Methoxy-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (20).** Following general procedure B, 4-methoxy-1,2-diaminobenzene (84 mg) was allowed to react for 7 h at rt to give 90.2 mg of the crude title compound (44% yield) as a gray powder: mp >260 °C;  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ )  $\delta$  7.96 (d,  $J$  = 8.0 Hz, 2 H), 7.62 (d,  $J$  = 8.0 Hz, 2 H), 7.44 (d,  $J$  = 8.5 Hz, 1 H), 7.07 (d,  $J$  = 2.5 Hz, 1 H), 6.80 (dd,  $J$  = 8.5, 2.5 Hz, 1 H), 3.80 (s, 3 H);  $^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ )  $\delta$  157.1, 153.5, 132.9, 128.2, 125.3, 116.5, 112.1, 98.2, 55.9;  $^{19}\text{F}$  NMR (470 MHz, acetone- $d_6$ )  $\delta$  -142.7;  $^{11}\text{B}$  NMR (128 MHz, acetone- $d_6$ )  $\delta$  4.0; FTIR (neat)  $\nu$  2966, 2880, 2364, 1628, 1438, 1211, 965, 941, 832; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{11}\text{N}_2\text{OBF}_3$  ( $\text{M} - \text{K}$ ) $^-$  291.0917, found 291.0936.

## Cross Couplings of Benzimidazole-Substituted Potassium Organotrifluoroborates

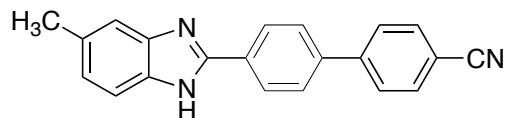
### General Procedure C.

A microwave vial was charged with bromide (0.25 mmol), benzimidazole (0.26 mmol), Pd(OAc)<sub>2</sub> (2.80 mg, 12.5 μmol), XPhos (12 mg, 25 μmol), and Et<sub>3</sub>N (70 μL, 0.50 mmol). The reaction vessel was sealed, then evacuated and backfilled with argon 3 times. After dissolving the reaction mixture in 1.4 mL of degassed EtOH, the reaction mixture was allowed to stir at 85 °C for 16 h. The mixture was filtered through Celite and the filter cake was washed with EtOAc (6 mL). The filtrate was concentrated and purified on a silica gel column to yield pure product.



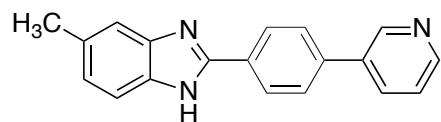
**2-(4'-Methoxy-[1,1'-biphenyl]-4-yl)-5-**

**methyl-1H-benzo[d]imidazole.** Following general procedure C, 4-bromoanisole (47 mg, 32 μL) and **2a** (82 mg) were allowed to react to give 62.9 mg of the title compound (80% yield) as a white solid: mp 251–256 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.11 (d, *J* = 8.5 Hz, 2 H), 7.61 (d, *J* = 8.0 Hz, 2 H), 7.53 (d, *J* = 8.5 Hz, 2 H), 7.32–7.55 (m, 2 H), 7.08 (d, *J* = 8.0 Hz, 1 H), 6.96 (d, *J* = 8.5 Hz, 2 H), 3.84 (s, 3 H), 2.46 (s, 3 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 159.7, 151.5, 142.4, 132.7, 128.3, 128.2, 127.3, 127.1, 124.6, 114.5, 55.5, 21.9; FTIR (neat) ν 2930, 1636, 1410, 1216, 967, 852, 776; HRMS (ESI) *m/z* calcd for C<sub>21</sub>H<sub>19</sub>N<sub>2</sub>O (MH)<sup>+</sup> 315.1497, found 315.1488.



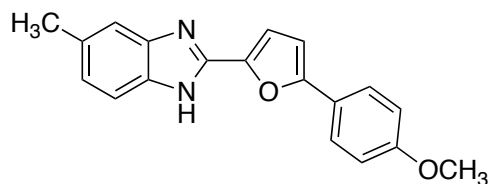
**4'-(5-Methyl-1H-benzo[d]imidazol-2-yl)-**

**[1,1'-biphenyl]-4-carbonitrile.** Following general procedure C, 4-bromobenzonitrile (46 mg) and **2a** (82 mg) were allowed to react to give 68.1 mg of the title compound (88% yield) as an off-white solid: mp >260 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17 (d,  $J$  = 8.5 Hz, 2 H), 7.73 (d,  $J$  = 8.5 Hz, 2 H), 7.68 (d,  $J$  = 8.5 Hz, 2 H), 7.65 (d,  $J$  = 8.5 Hz, 2 H), 7.50–7.60 (m, 1 H), 7.37–7.47 (m, 1 H), 7.11 (d,  $J$  = 8.0 Hz, 1 H), 2.47 (s, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.7, 144.6, 140.5, 132.8, 130.3, 127.9, 127.7, 127.3, 124.9, 120.4, 118.9, 111.5, 21.9; FTIR (neat)  $\nu$  2930, 2251, 1636, 1410, 1216, 967, 852; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{16}\text{N}_3$  (MH) $^+$  310.1344, found 310.1335.

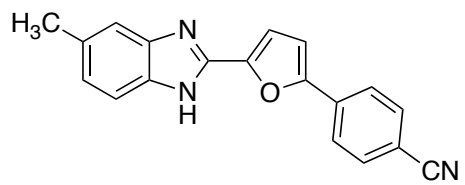


**5-Methyl-2-(4-(pyridin-3-yl)phenyl)-1H-**

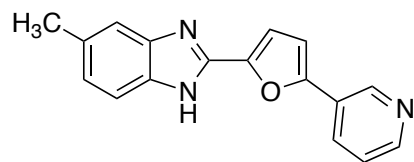
**benzo[d]imidazole.** Following general procedure C, 3-bromopyridine (40 mg, 25  $\mu\text{L}$ ) and **2a** (82 mg) were allowed to react to give 44.6 mg of the title compound (63% yield) as a light-yellow solid: mp >260 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  8.86 (d,  $J$  = 2.0 Hz, 1 H), 8.54 (dd,  $J$  = 4.5, 1.5 Hz, 1 H), 8.16 (dt,  $J$  = 8.5, 2.0 Hz, 2 H), 8.13 (ddd,  $J$  = 8.0, 2.0, 1.5 Hz, 1 H), 7.81 (dt,  $J$  = 8.5, 2.0 Hz, 2 H), 7.52 (ddd,  $J$  = 8.0, 4.5, 1.0 Hz, 1 H), 7.48 (d,  $J$  = 8.0 Hz, 1 H), 7.38 (s, 1 H), 7.09 (dd,  $J$  = 8.5, 1.0 Hz, 1 H), 2.46 (s, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  152.3, 149.2, 148.3, 140.0, 137.6, 136.5, 134.1, 131.0, 128.7, 128.4, 125.6, 125.5, 21.8; FTIR (neat)  $\nu$  2926, 1646, 1416, 1196, 933, 852; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{16}\text{N}_3$  (MH) $^+$  286.1344, found 286.1135.



**2-(5-(4-Methoxyphenyl)furan-2-yl)-5-methyl-1H-benzo[d]imidazole.** Following general procedure C, 4-bromoanisole (47 mg, 32  $\mu$ L) and **2e** (79 mg) were allowed to react to give 43.4 mg of the title compound (58% yield) as an off-white solid: mp 211–213  $^{\circ}$ C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J$  = 8.0 Hz, 1 H), 7.51 (d,  $J$  = 8.5 Hz, 2 H), 7.42 (s, 1 H), 7.20 (d,  $J$  = 4.0 Hz, 1 H), 7.08 (d,  $J$  = 8.5 Hz, 1 H), 6.81 (d,  $J$  = 8.5 Hz, 2 H), 6.57 (d,  $J$  = 3.5 Hz, 1 H), 3.77 (s, 3 H), 2.46 (s, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7, 155.5, 144.3, 144.1, 133.1, 125.8, 124.7, 123.0, 114.3, 113.0, 106.3, 55.4, 21.8; FTIR (neat)  $\nu$  2930, 1624, 1417, 1220, 967, 837; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{17}\text{N}_2\text{O}_2$  (MH) $^{+}$  305.1290, found 305.1284.



**4-(5-(5-Methyl-1H-benzo[d]imidazol-2-yl)furan-2-yl)benzonitrile.** Following general procedure C, 4-bromobenzonitrile (46 mg) and **2e** (79 mg) were allowed to react to give 53.3 mg of the title compound (71% yield) as an off-white solid: mp 227–230  $^{\circ}$ C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (d,  $J$  = 8.5 Hz, 2 H), 7.50 (d,  $J$  = 8.5 Hz, 2 H), 7.43–7.55 (m, 2 H), 7.24 (d,  $J$  = 3.5 Hz, 1 H), 7.14 (dd,  $J$  = 8.5, 1.0 Hz, 1 H), 6.87 (d,  $J$  = 3.5 Hz, 1 H), 2.48 (s, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  153.0, 146.5, 143.2, 133.7, 132.6, 125.3, 124.3, 118.8, 112.8, 111.0, 110.7, 21.9; FTIR (neat)  $\nu$  2926, 2248, 1626, 1416, 1216, 956, 852; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{14}\text{N}_3\text{O}$  (MH) $^{+}$  300.1137, found 300.1127.



**5-Methyl-2-(5-(pyridin-3-yl)furan-2-yl)-1H-**

**benzo[d]imidazole.** Following general procedure C, 3-bromopyridine (40 mg, 25  $\mu$ L) and **2e** (79 mg) were allowed to react to give 45.2 mg of the title compound (66% yield) as a light-yellow solid: mp >260  $^{\circ}$ C;  $^1$ H NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.82 (s, 1 H), 8.38 (d,  $J$  = 5.0 Hz, 1 H), 7.63 (d,  $J$  = 8.0 Hz, 1 H), 7.20 (d,  $J$  = 4.0 Hz, 1 H), 7.10–7.60 (m, 2 H), 7.08 (dd,  $J$  = 8.0, 4.5 Hz, 1 H), 7.01 (d,  $J$  = 8.0 Hz, 1 H), 6.75 (d,  $J$  = 3.5 Hz, 1 H), 2.39 (s, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  151.5, 148.0, 146.3, 144.8, 143.6, 133.1, 131.4, 126.3, 124.7, 123.8, 112.4, 109.4, 21.8; FTIR (neat)  $\nu$  2921, 1636, 1430, 1222, 960, 852; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{14}\text{N}_3\text{O}$  (MH) $^{+}$  276.1137, found 276.1126.

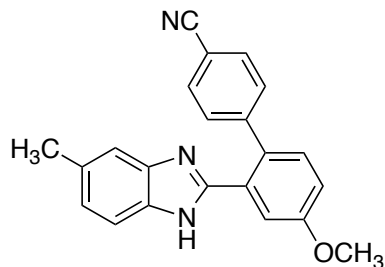
## Sequential Oxidative Condensation/Cross Couplings to Form Substituted Benzimidazoles

### General Procedure D.

A microwave vial was charged with 75 mg (0.60 mmol) of 3,4-diaminotoluene and dissolved in 3.2 mL of a 1:1 EtOH/MeCN mixture. To this solution was added 12  $\mu$ L (0.06 mmol) of a saturated aqueous  $\text{KHF}_2$  solution. The reaction mixture was purged with  $\text{O}_2$  for 20 seconds before allowing the reaction to stir for 2 min under positive  $\text{O}_2$  pressure. The oxygenated reaction mixture was then charged with 0.60 mmol of the required trifluoroborate. The reaction was allowed to stir for the indicated time, at the

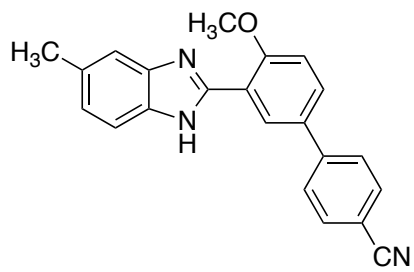


indicated temperature, until judged complete by  $^1\text{H}$  NMR. The reaction was concentrated and triturated with  $\text{Et}_2\text{O}$ . To the crude reaction residue was then added 4-bromobenzonitrile (93 mg, 0.50 mmol),  $\text{Pd}(\text{OAc})_2$  (6.7 mg, 30  $\mu\text{mol}$ ), XPhos (28 mg, 60  $\mu\text{mol}$ ), and  $\text{Et}_3\text{N}$  (140  $\mu\text{L}$ , 1.0 mmol). The reaction vessel was sealed, then evacuated and backfilled with argon 3 times. After dissolving the reaction mixture in 3 mL of degassed  $\text{EtOH}$ , the reaction mixture was allowed to stir at 85  $^\circ\text{C}$  for 16 h. The mixture was filtered through Celite and the filter cake was washed with  $\text{EtOAc}$  (8 mL). The filtrate was concentrated and purified on a silica gel column to yield pure product.

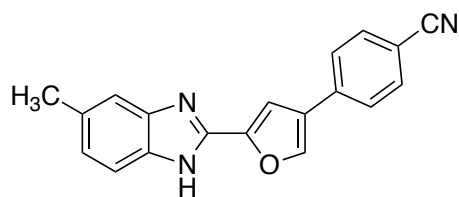


**4'-Methoxy-2'-(5-methyl-1H-benzo[d]imidazol-2-**

**yl)-[1,1'-biphenyl]-4-carbonitrile (5a).** Following general procedure D, potassium (2-formyl-4-methoxyphenyl)trifluoroborate<sup>1</sup> (145 mg) was allowed to react to give 69.1 mg of the title compound (41% yield) as a colorless oil:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20 (d,  $J = 2.5$  Hz, 1 H), 7.18 (d,  $J = 2.5$  Hz, 1 H), 7.17–7.21 (m, 1 H), 7.08 (d,  $J = 8.5$  Hz, 1 H), 7.03 (d,  $J = 3.0$  Hz, 1 H), 7.01 (dd,  $J = 8.5, 1.5$  Hz, 1 H), 6.97 (dd,  $J = 8.5, 3.0$  Hz, 1 H), 6.88 (s, 1 H), 6.86 (s, 1 H), 6.85–6.89 (m, 1 H), 3.69 (s, 3 H), 2.40 (s, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.6, 151.0, 144.8, 133.0, 131.8, 131.6, 130.3, 129.5, 124.6, 118.8, 116.3, 116.0, 110.4, 55.5, 21.7; FTIR (neat)  $\nu$  2924, 2244, 1632, 1434, 1266, 1183, 981, 955, 813 ; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}$  (MH)<sup>+</sup> 340.1450, found 340.1457.

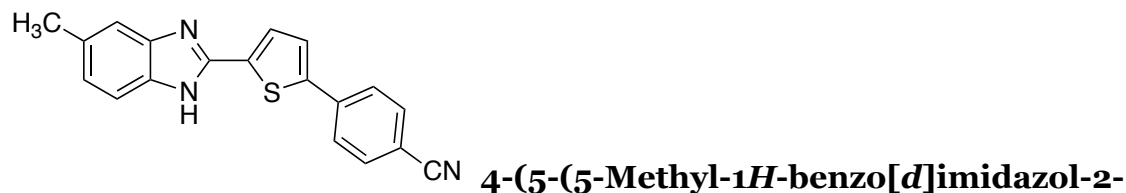


**4'-Methoxy-3'-(5-methyl-1H-benzo[d]imidazol-2-yl)-[1,1'-biphenyl]-4-carbonitrile (5b).** Following general procedure D, potassium (3-formyl-4-methoxyphenyl)trifluoroborate<sup>1</sup> (145 mg) was allowed to react to give 88.3 mg of the title compound (52% yield) as a colorless oil: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 10.63 (d, *J* = 2.5 Hz, 1 H), 8.83 (d, *J* = 2.5 Hz, 1 H), 7.75 (dt, *J* = 8.5, 2.0 Hz, 2 H), 7.69 (dt, *J* = 8.5, 2.0 Hz, 2 H), 7.67–7.76 (m, 1 H), 7.62 (dd, *J* = 8.5, 2.5 Hz, 1 H), 7.31–7.40 (m, 1 H), 7.15 (d, *J* = 9.0 Hz, 1 H), 7.11 (d, *J* = 7.5 Hz, 1 H), 4.12 (s, 3 H), 2.50 (s, 3 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 157.1, 144.4, 132.7, 129.5, 127.6, 119.1, 112.3, 110.8, 56.4, 21.9; FTIR (neat) ν 2926, 2248, 1626, 1416, 1216, 956, 852; HRMS (ESI) *m/z* calcd for C<sub>22</sub>H<sub>18</sub>N<sub>3</sub>O (MH)<sup>+</sup> 340.1450, found 340.1488.

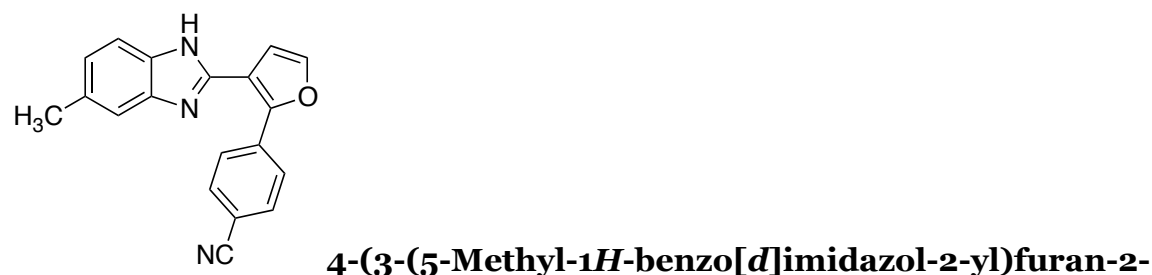


**4-(5-(5-Methyl-1H-benzo[d]imidazol-2-yl)furan-3-yl)benzonitrile (5c).** Following general procedure D, potassium (5-formylfuran-3-yl)trifluoroborate<sup>2</sup> (121 mg) was allowed to react to give 103 mg of the title compound (69% yield) as a light-yellow oil: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.16 (s, 1 H), 7.57–7.64 (m, 4 H), 7.46 (d, *J* = 8.0 Hz, 1 H), 7.33 (s, 1 H), 7.32 (s, 1 H), 7.06 (d, *J* = 8.0 Hz, 1 H), 2.41 (s, 3 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 153.6, 133.5, 132.8, 125.2, 124.3,

118.8, 111.4, 106.5, 21.8; FTIR (neat)  $\nu$  2944, 2238, 1628, 1434, 1216, 966, 851 ; HRMS (ESI)  $m/z$  calcd for  $C_{19}H_{14}N_3O$  (MH)<sup>+</sup> 300.1137, found 300.1147.

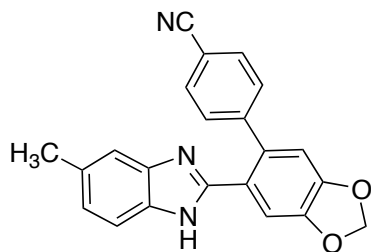


Following general procedure D, potassium (5-formylthiophen-2-yl)trifluoroborate<sup>2</sup> (131 mg) was allowed to react to give 104 mg of the title compound (66% yield) as a yellow oil: <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD)  $\delta$  7.87 (dt,  $J$  = 8.5, 2.0 Hz, 2 H), 7.75 (dt,  $J$  = 9.0, 2.0 Hz, 2 H), 7.72 (d,  $J$  = 4.0 Hz, 1 H), 7.63 (d,  $J$  = 4.0 Hz, 1 H), 7.45 (d,  $J$  = 8.0 Hz, 1 H), 7.35 (s, 1 H), 7.10 (dd,  $J$  = 8.5, 1.0 Hz, 1 H), 2.47 (s, 3 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  147.7, 145.3, 139.3, 135.4, 134.1, 129.1, 127.5, 127.3, 119.5, 112.2, 21.7; FTIR (neat)  $\nu$  2920, 2245, 1631, 1454, 1277, 1183, 989, 950, 813; HRMS (ESI)  $m/z$  calcd for  $C_{19}H_{14}N_3O$  (MH)<sup>+</sup> 316.0908, found 316.0921.



Following general procedure D, potassium (3-formylfuran-2-yl)trifluoroborate<sup>2</sup> (121 mg) was allowed to react to give 82.5 mg of the title compound (55% yield) as a light-yellow oil: <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD)  $\delta$  7.98 (dt,  $J$  = 9.0, 1.5 Hz, 2 H), 7.83 (d,  $J$  = 1.5 Hz, 1 H), 7.74 (dt,  $J$  = 8.5, 2.0 Hz, 2 H), 7.28–7.56 (m, 2 H), 7.13 (d,

$J = 8.0$  Hz, 1 H), 6.96 (d,  $J = 1.5$  Hz, 1 H), 2.48 (s, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  151.2, 145.2, 135.6, 133.6, 127.8, 119.6, 116.1, 114.7, 112.7, 21.7; FTIR (neat)  $\nu$  2926, 2248, 1626, 1416, 1216, 956, 852; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{14}\text{N}_3\text{O}$  (MH) $^+$  300.1137, found 300.1140.



**4-(6-(5-Methyl-1H-benzo[d]imidazol-2-**

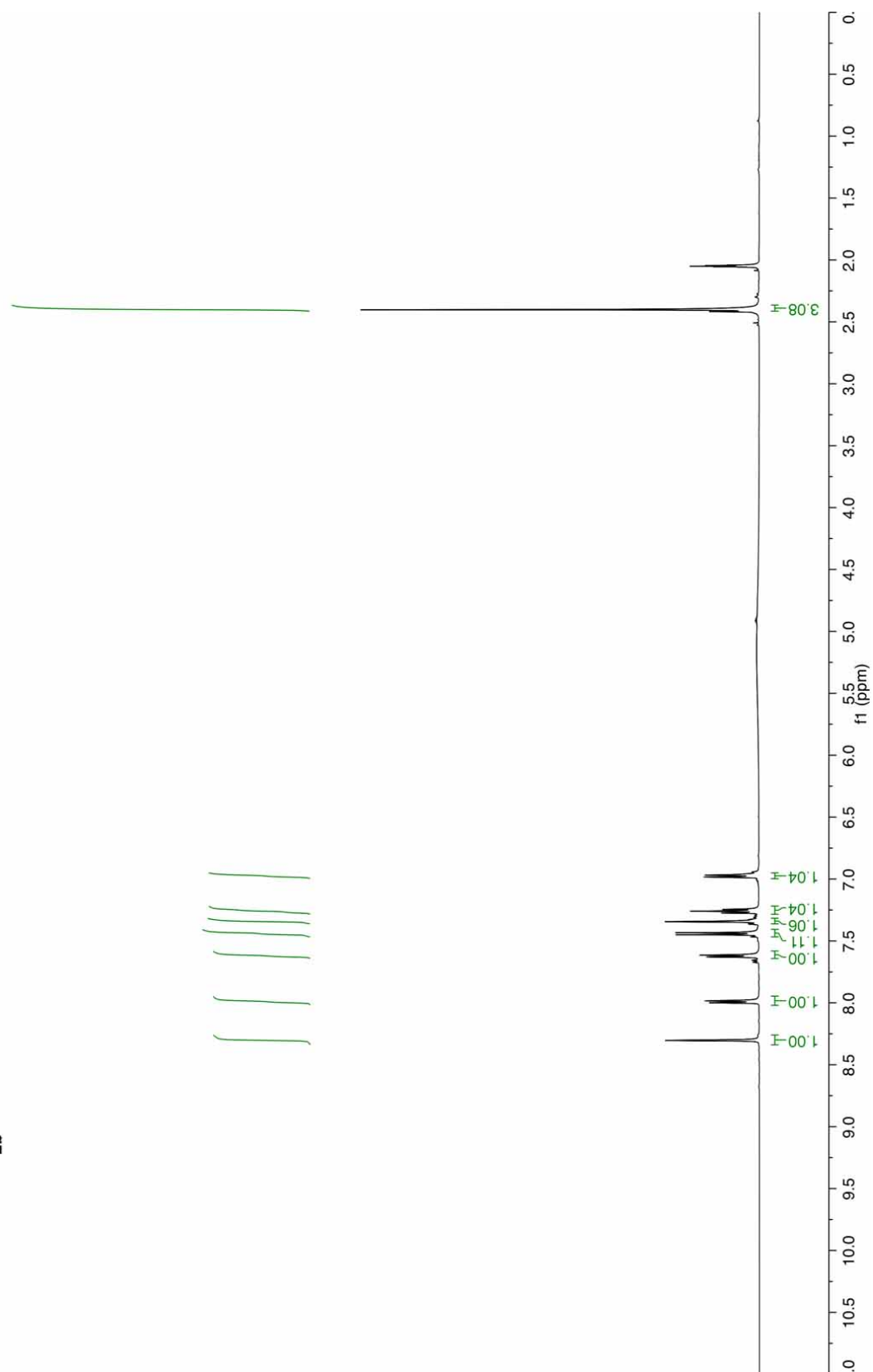
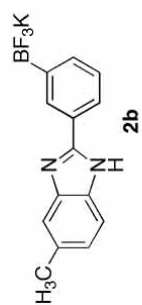
**yl)benzo[d][1,3]dioxol-5-yl)benzonitrile (5f).** Following general procedure D, potassium (6-formylbenzo[d][1,3]dioxol-5-yl)trifluoroborate<sup>5</sup> (154 mg) was allowed to react to give 77.4 mg of the title compound (44% yield) as a light-yellow oil:  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  7.48 (d,  $J = 8.5$  Hz, 2 H), 7.31 (d,  $J = 8.0$  Hz, 1 H), 7.23 (d,  $J = 8.5$  Hz, 2 H), 7.19 (s, 1 H), 7.18 (s, 1 H), 7.03 (dd,  $J = 8.0, 1.0$  Hz, 1 H), 6.99 (s, 1 H), 6.11 (s, 2 H), 2.41 (s, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  152.6, 151.0, 149.4, 146.3, 135.7, 133.8, 133.0, 131.1, 130.6, 125.3, 124.5, 121.2, 119.6, 118.5, 118.3, 111.6, 111.3, 103.6, 21.7; FTIR 2916, 2241, 1616, 1422, 1217, 940, 832; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{16}\text{N}_3\text{O}$  (MH) $^+$  354.1243, found 354.1258.

<sup>1</sup> Molander, G. A.; Figueroa, R. *J. Org. Chem.* **2006**, *71*, 6135-6140.

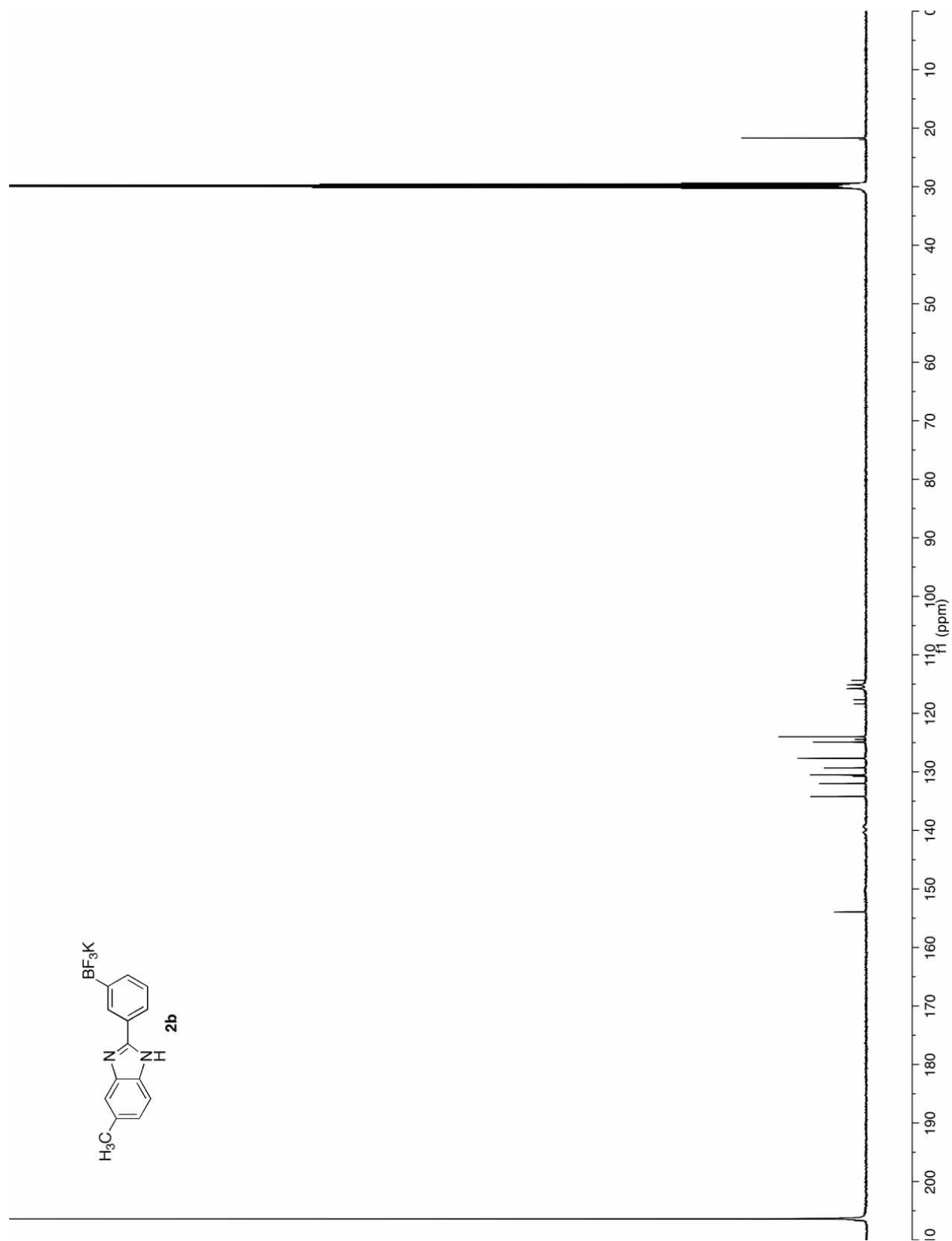
<sup>2</sup> Molander, G. A.; Cooper, D. J. *J. Org. Chem.* **2008**, *73*, 3885-3891.

<sup>3</sup> Molander, G. A.; Canturk, B.; Kennedy, L. E. *J. Org. Chem.* **2009**, *74*, 973-980.

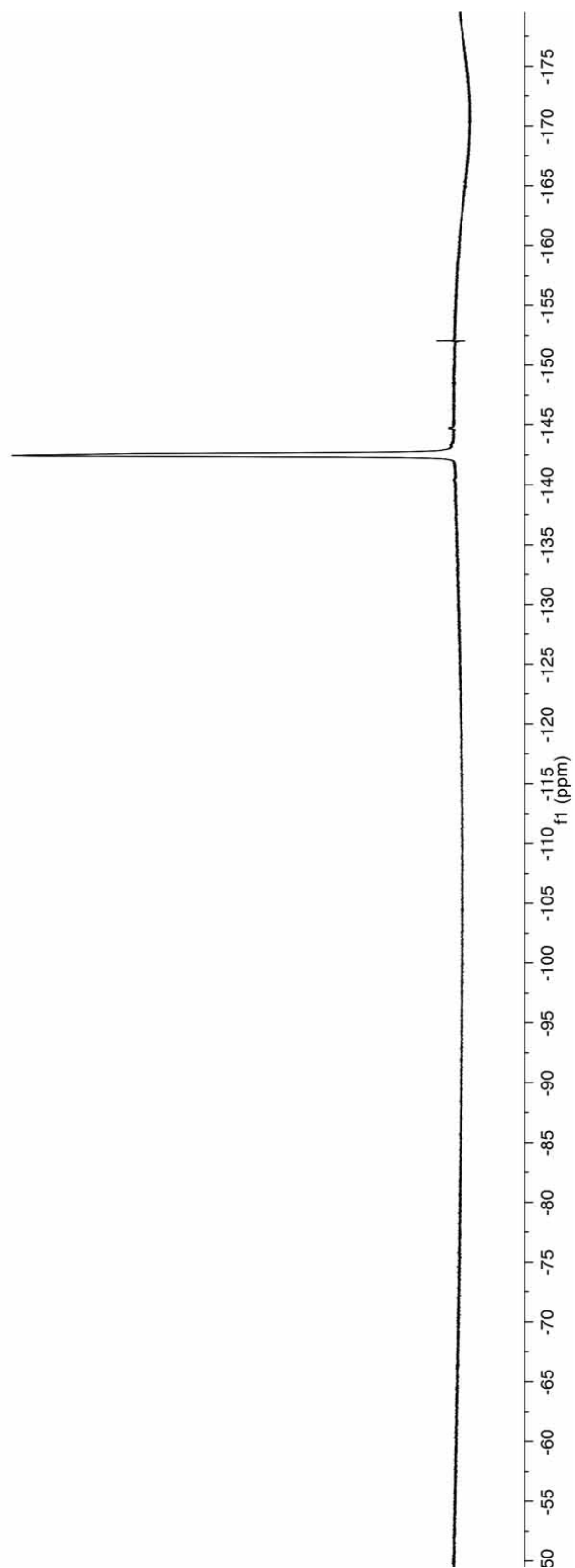
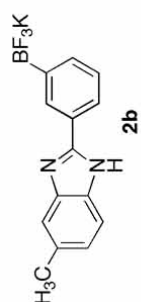
<sup>4</sup> Molander, G. A.; Febo-Ayala, W.; Jean-Gerard, L. *Org. Lett.* **2009**, *11*, 3830-3833.



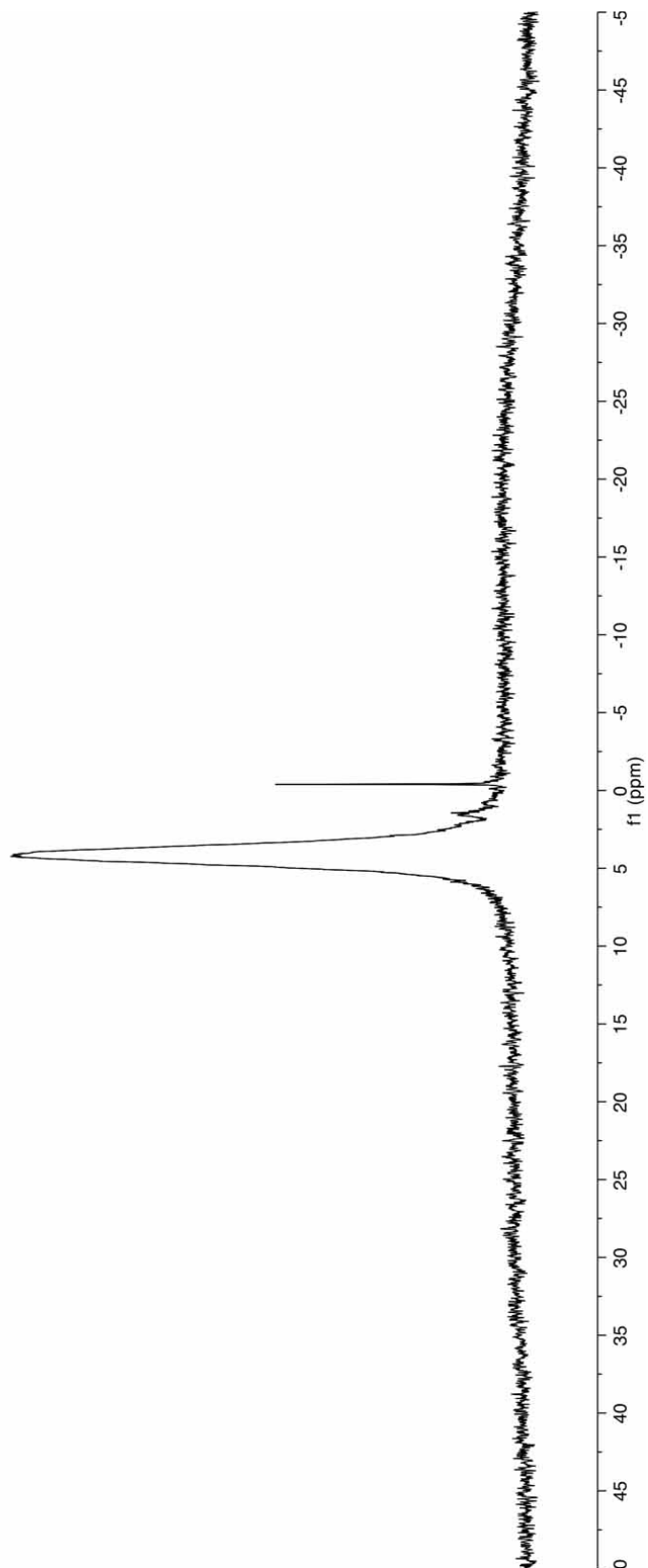
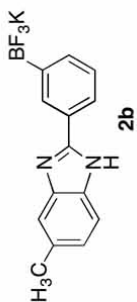
$^1\text{H}$  spectrum (500 MHz,  $\text{acetone-}d_6$ ) of potassium (3-(5-Methyl-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**2b**).



<sup>13</sup>C spectrum (125 MHz, acetone-*d*<sub>6</sub>) of potassium (3-(5-Methyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl)trifluoroborate (**2b**).

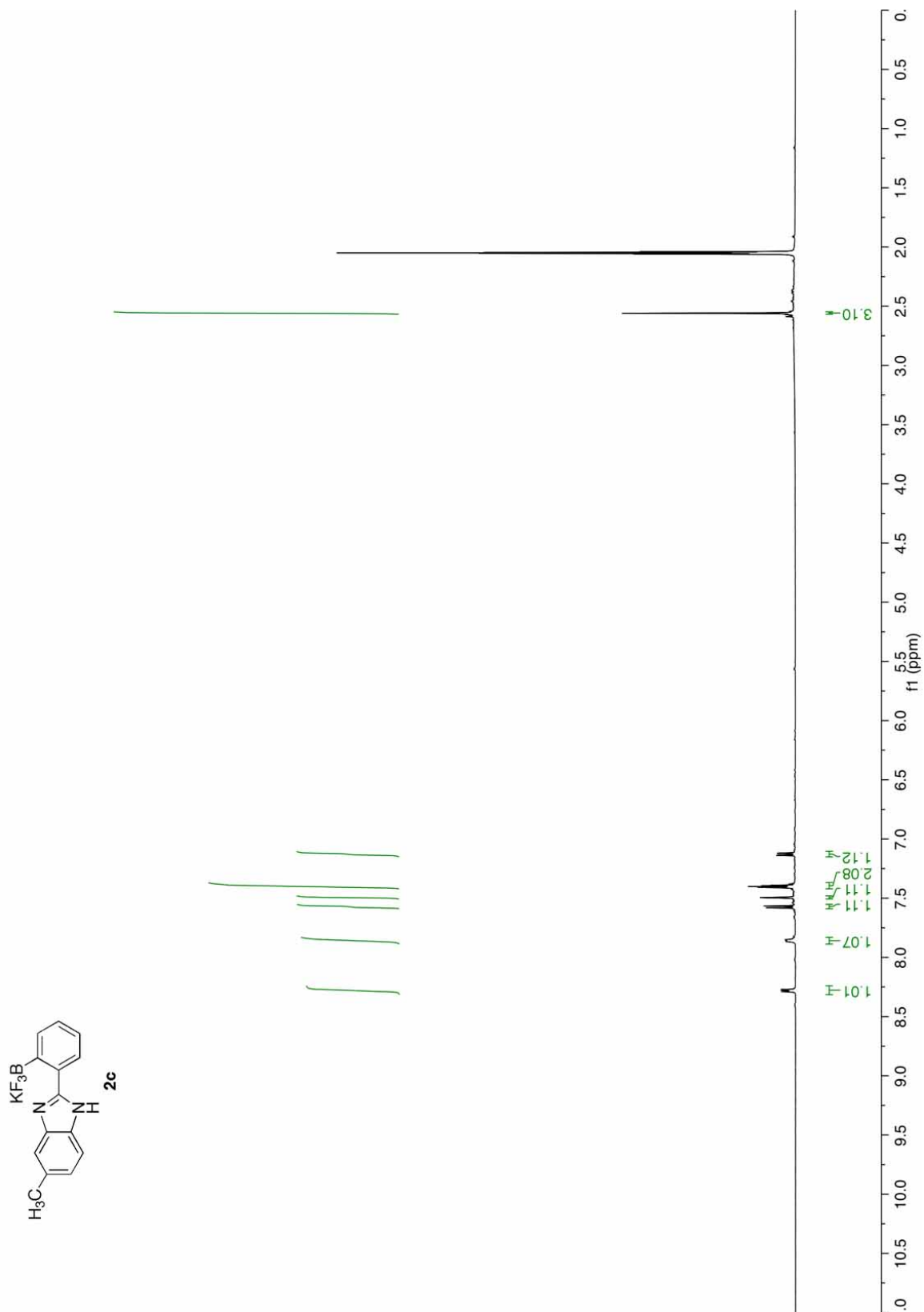


$^{19}\text{F}$  spectrum (470 MHz, acetone- $d_6$ ) of potassium (3-(5-Methyl-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**2b**).

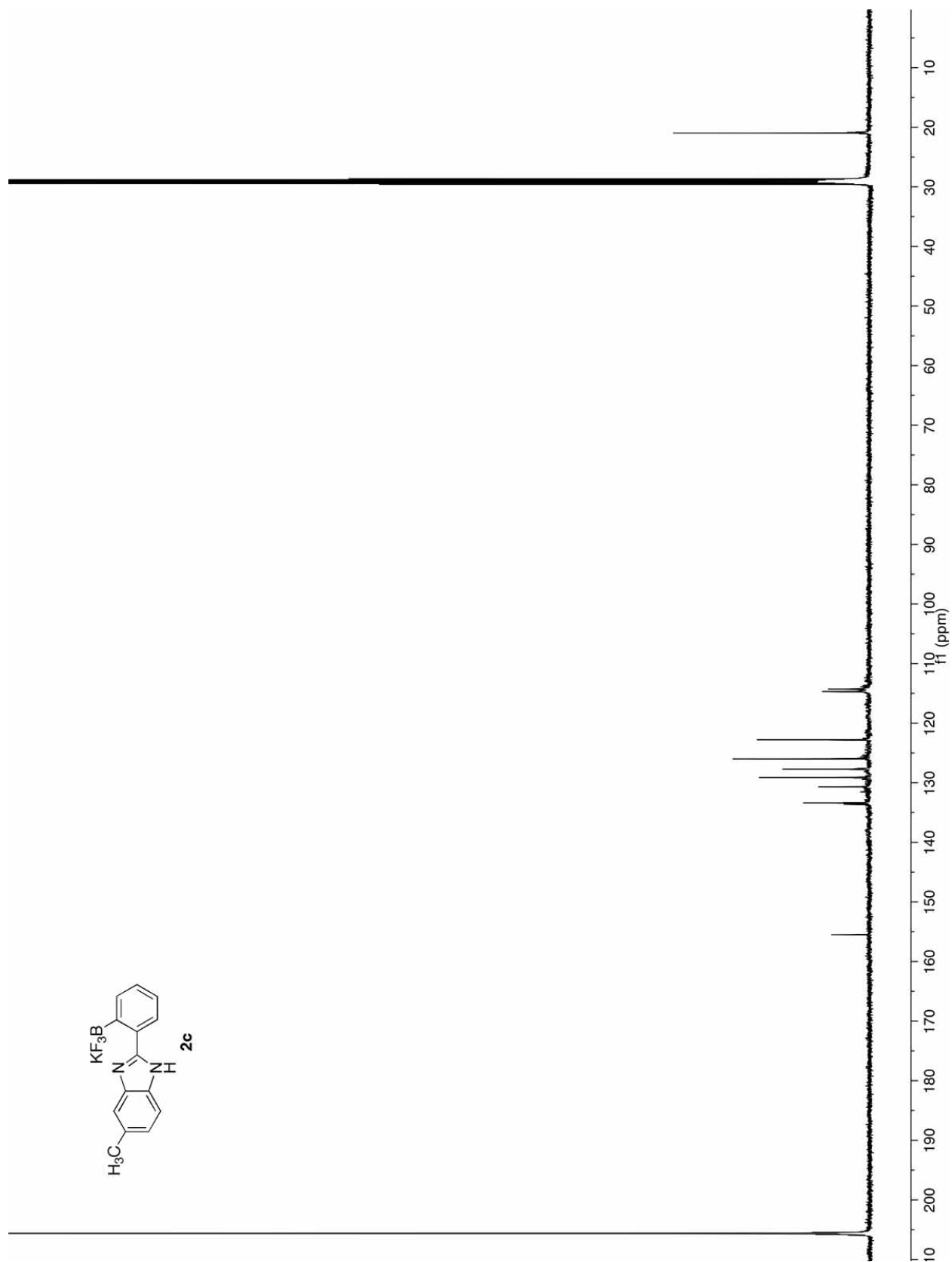


$^{11}\text{B}$  spectrum (128 MHz, acetone- $d_6$ ) of potassium (3-(5-Methyl-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**2b**).

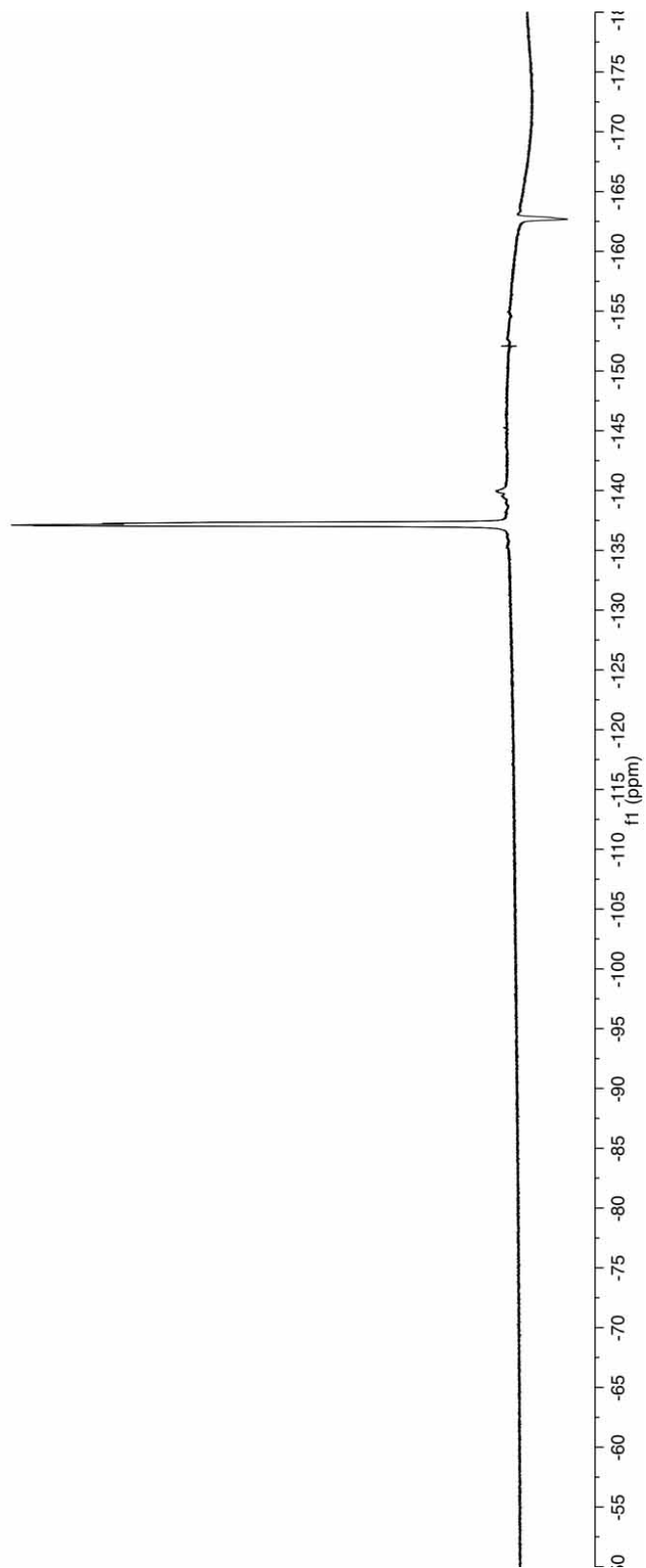
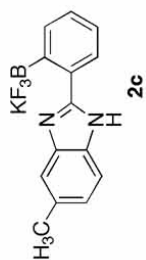




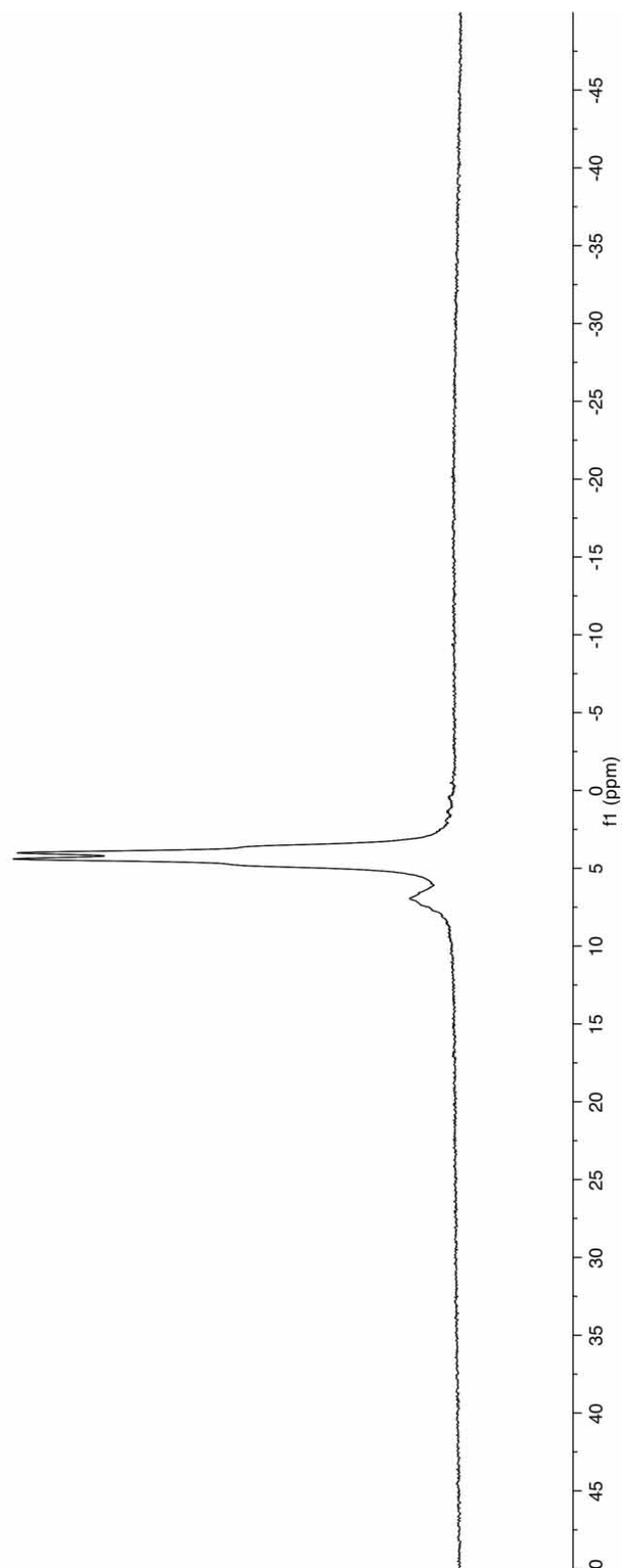
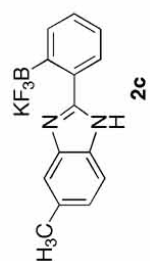
<sup>1</sup>H spectrum (500 MHz, acetone-*d*<sub>6</sub>) of potassium (2-(5-Methyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl)trifluoroborate (**2c**).



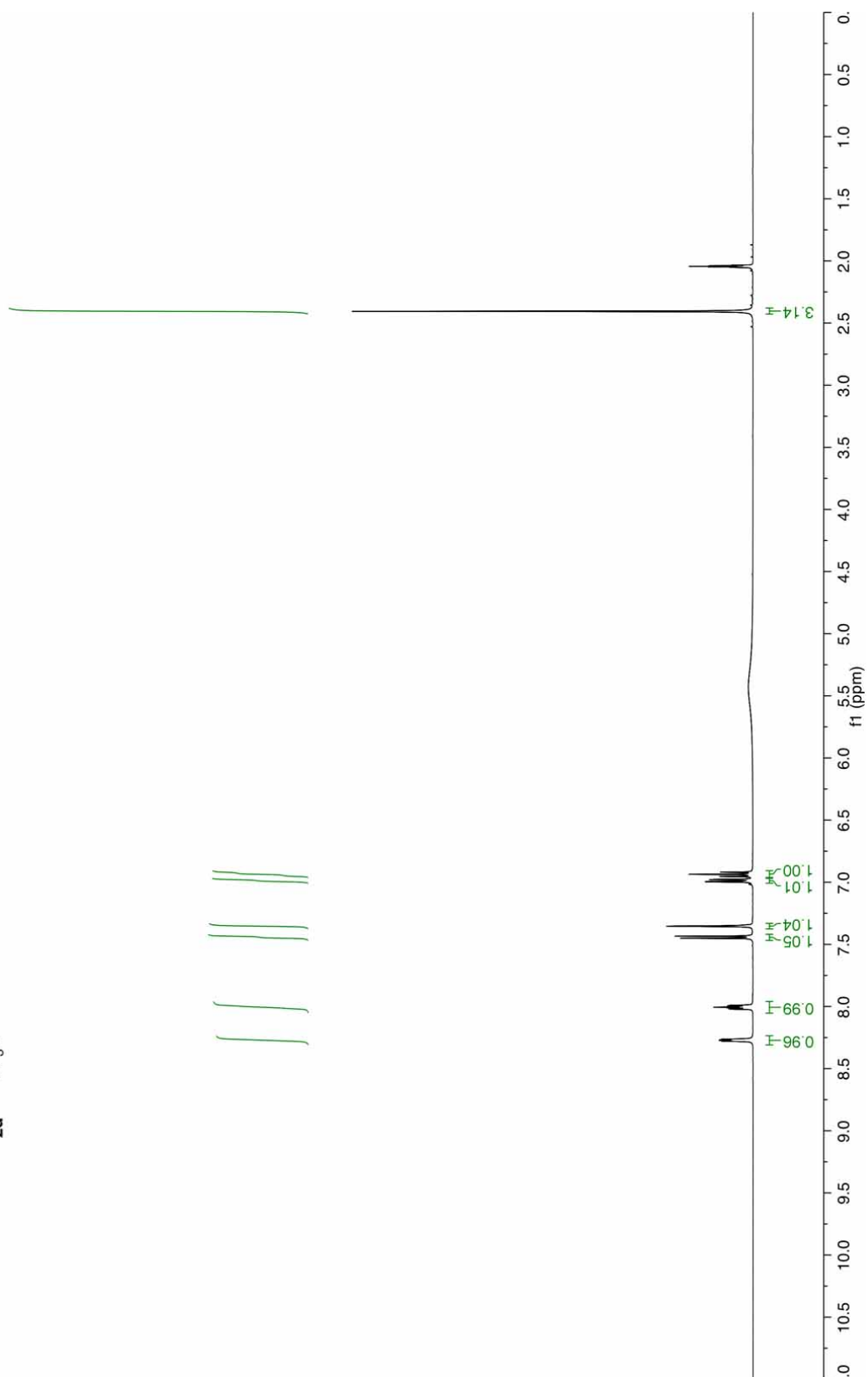
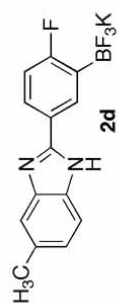
$^{13}\text{C}$  spectrum (125 MHz, acetone- $d_6$ ) of potassium (2-(5-Methyl-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**2c**).



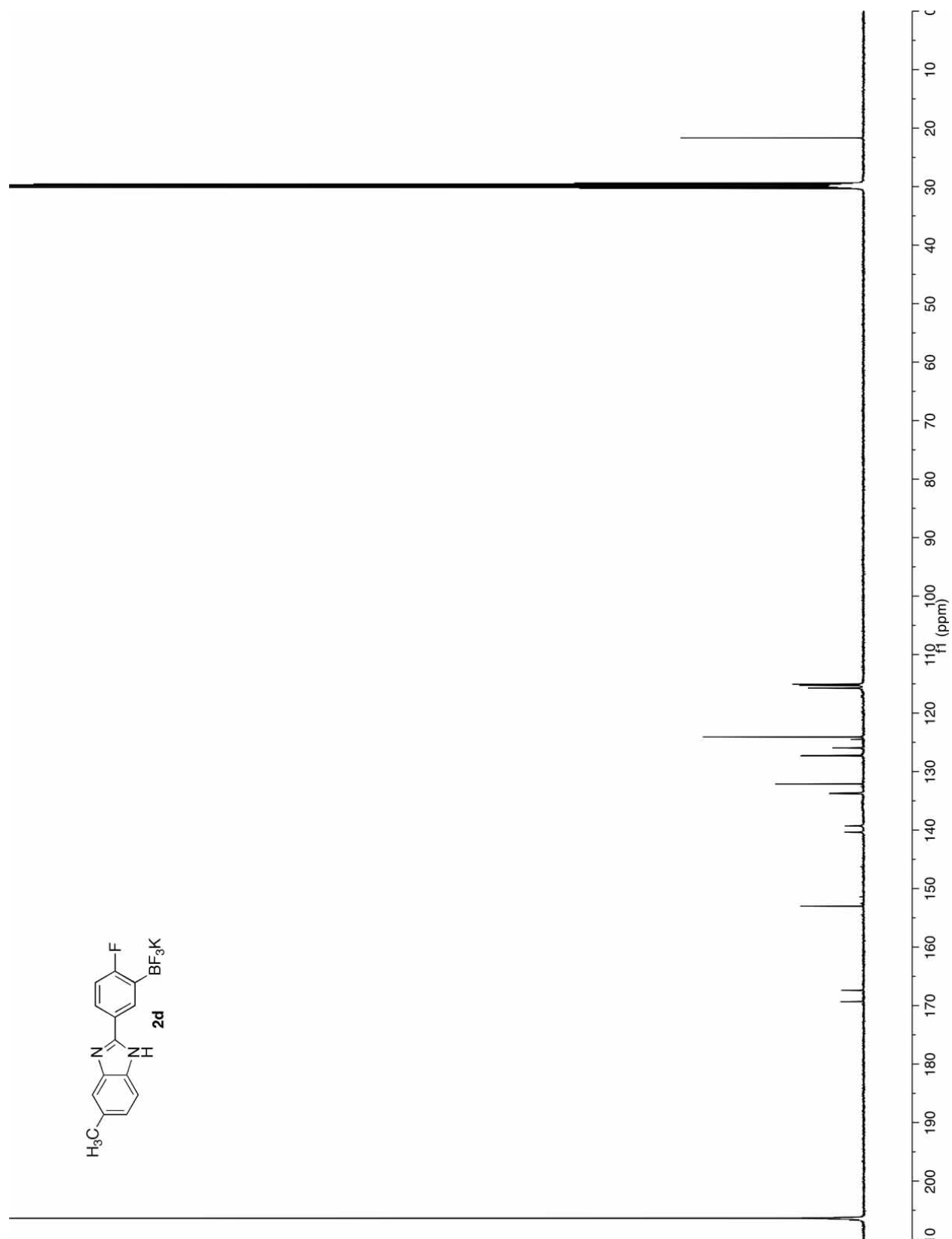
<sup>19</sup>F spectrum (470 MHz, acetone-*d*<sub>6</sub>) of potassium (2-(5-Methyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl)trifluoroborate (**2c**).



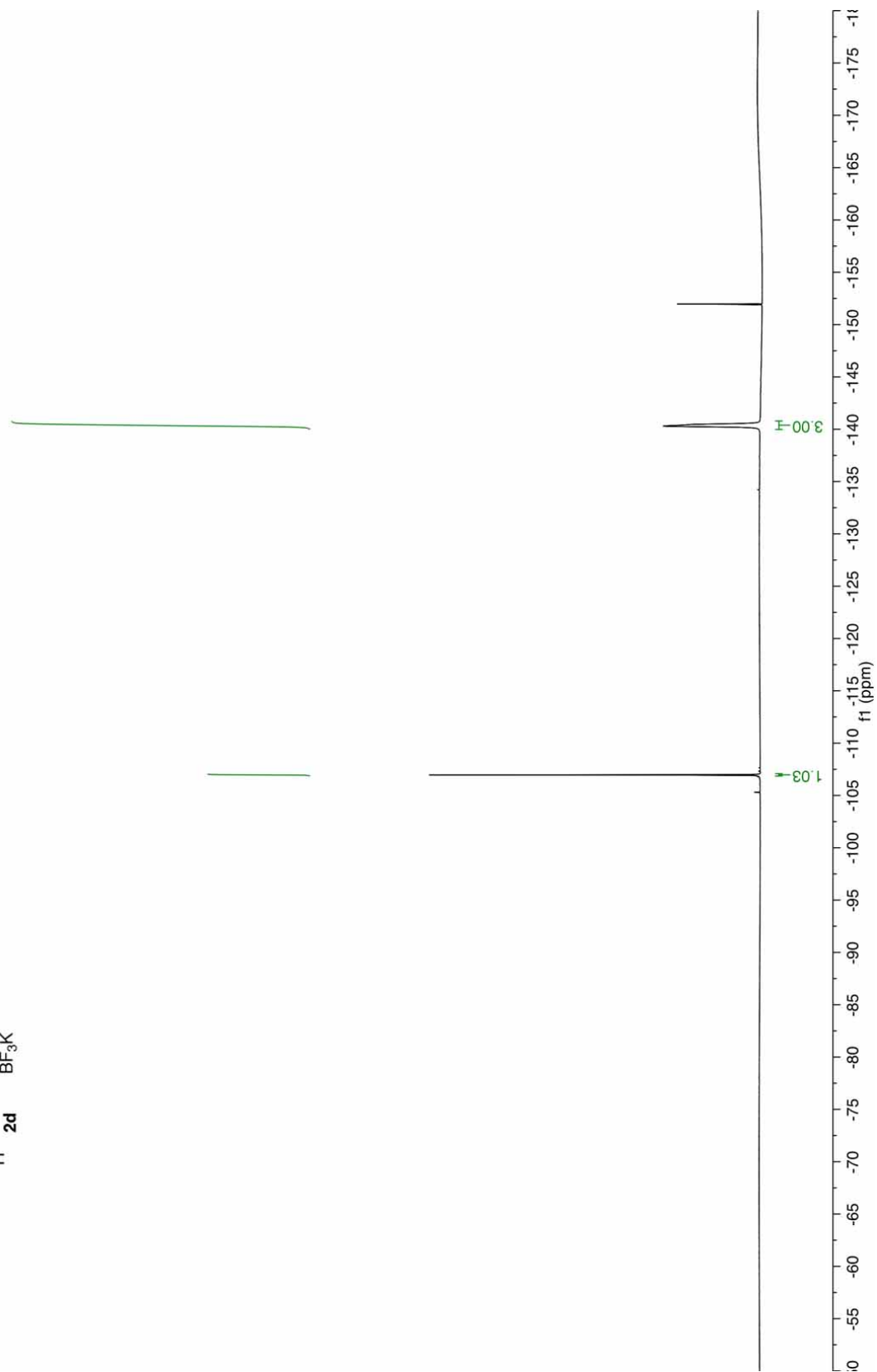
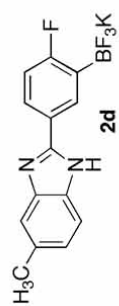
$^{11}\text{B}$  spectrum (128 MHz, acetone- $d_6$ ) of potassium (2-(5-Methyl-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**2c**).

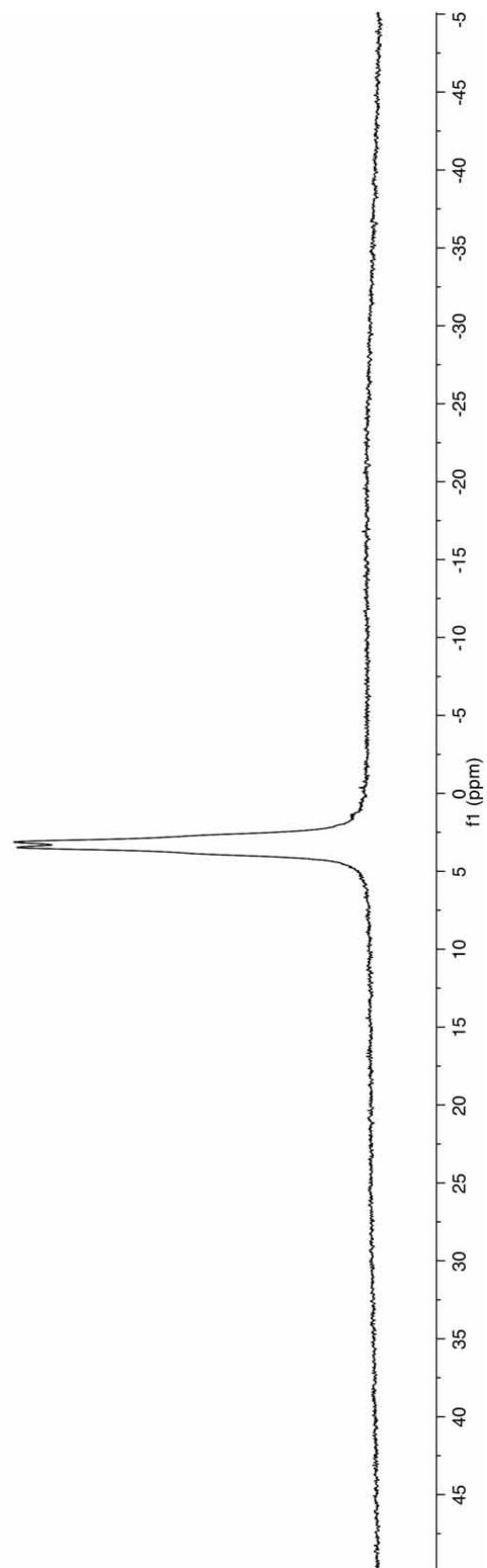
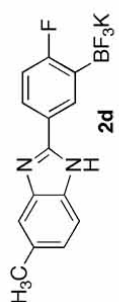


<sup>1</sup>H spectrum (500 MHz, acetone-*d*<sub>6</sub>) of potassium (2-Fluoro-5-(5-methyl-1H-benzo[*d*]imidazol-2-yl)phenyl)trifluoroborate (**2d**).



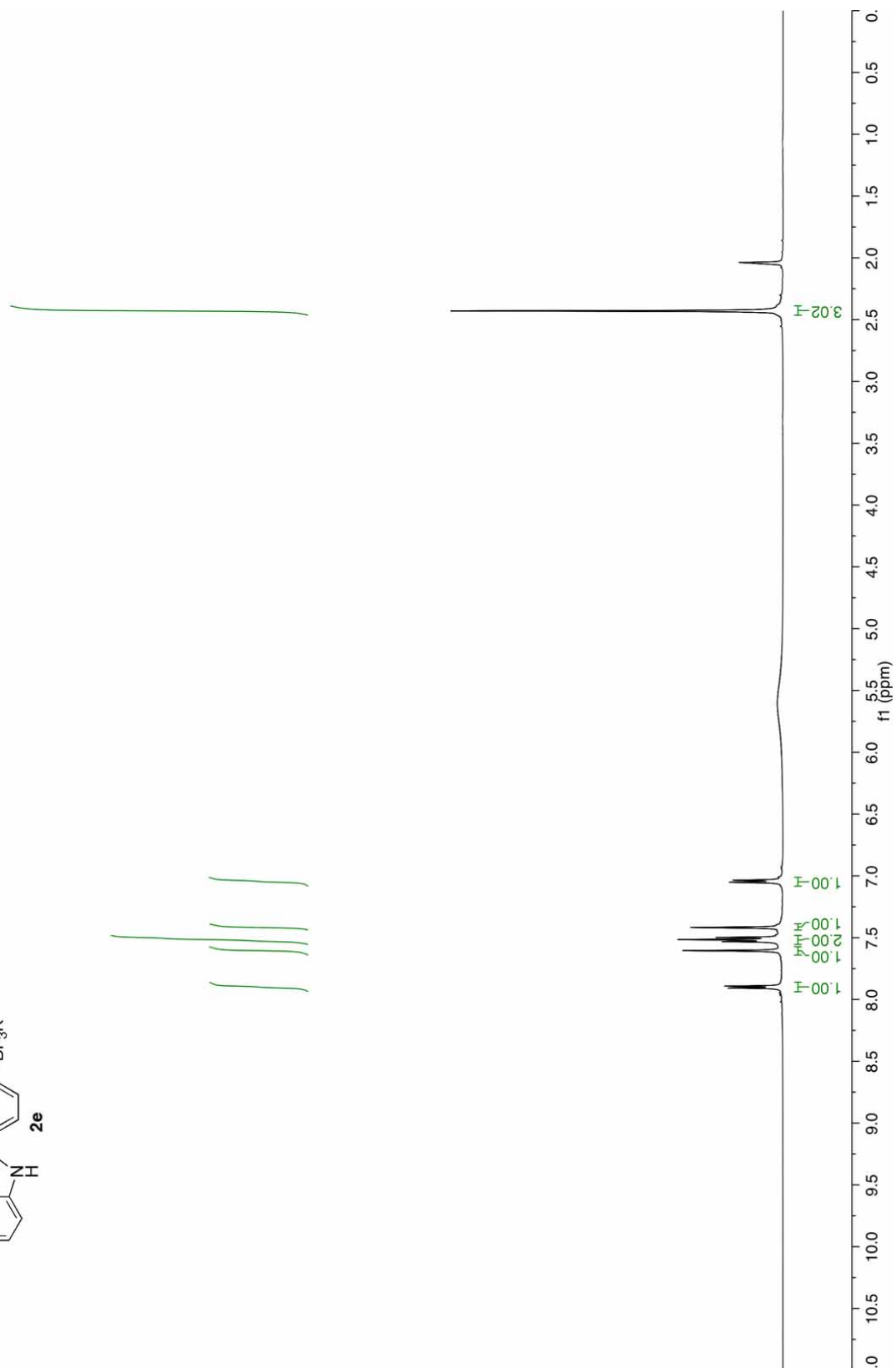
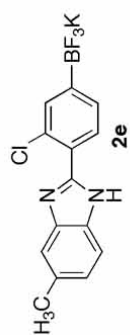
$^{13}\text{C}$  spectrum (125 MHz,  $\text{acetone-}d_6$ ) of potassium (2-Fluoro-5-(5-methyl-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**2d**).



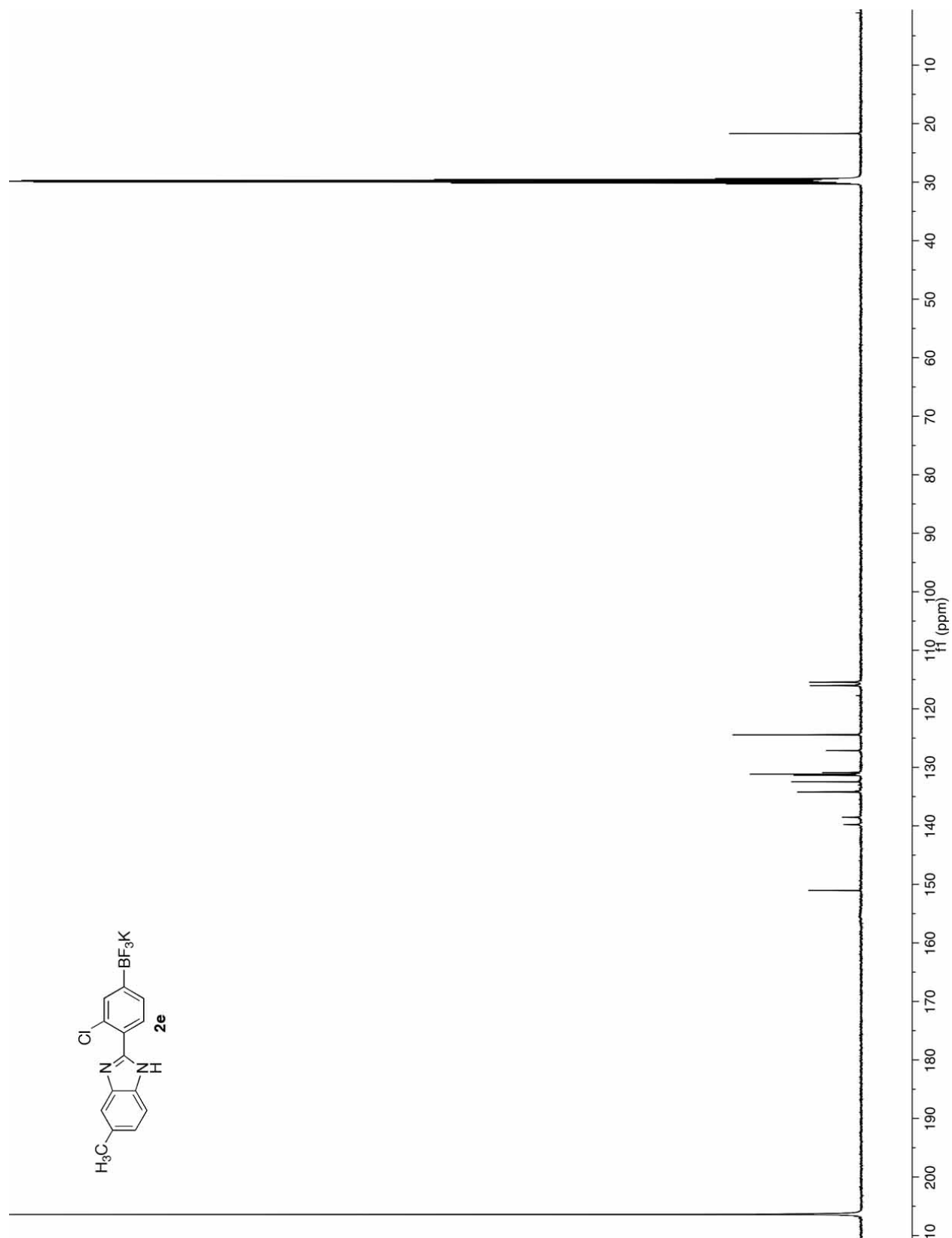


$^{11}\text{B}$  spectrum (128 MHz, acetone- $d_6$ ) of potassium (2-Fluoro-5-(5-methyl-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**2d**).

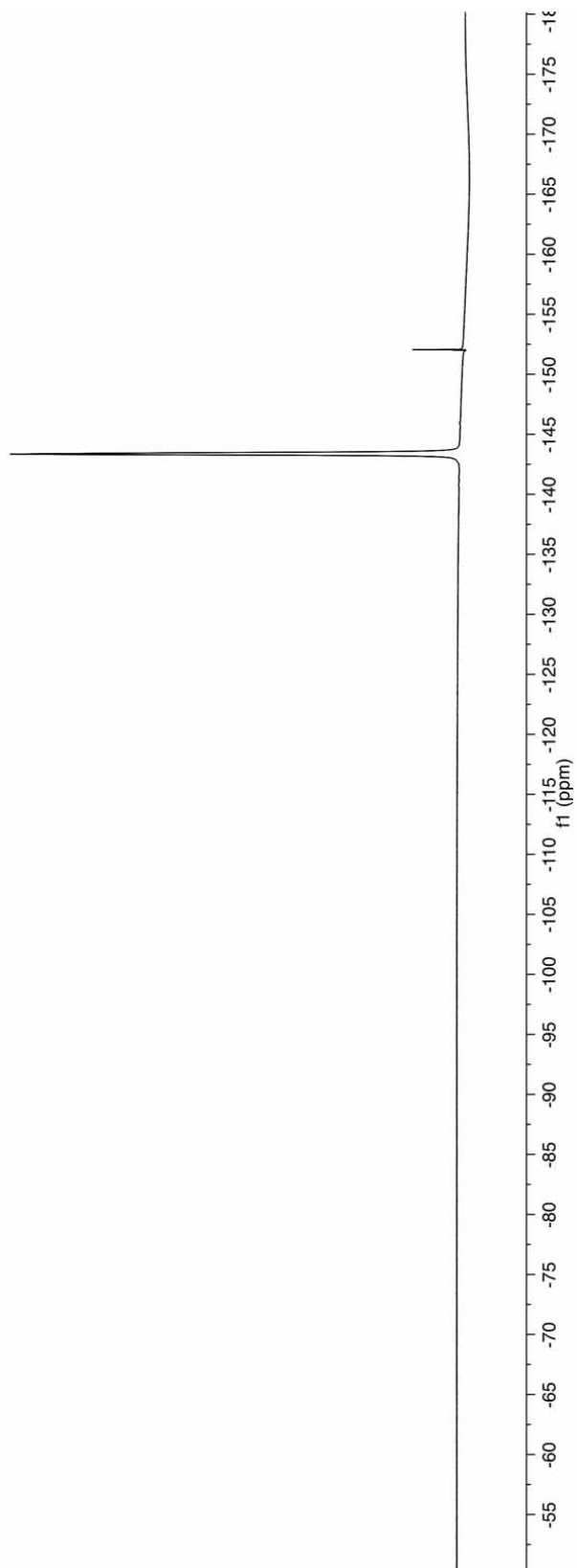
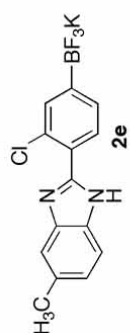




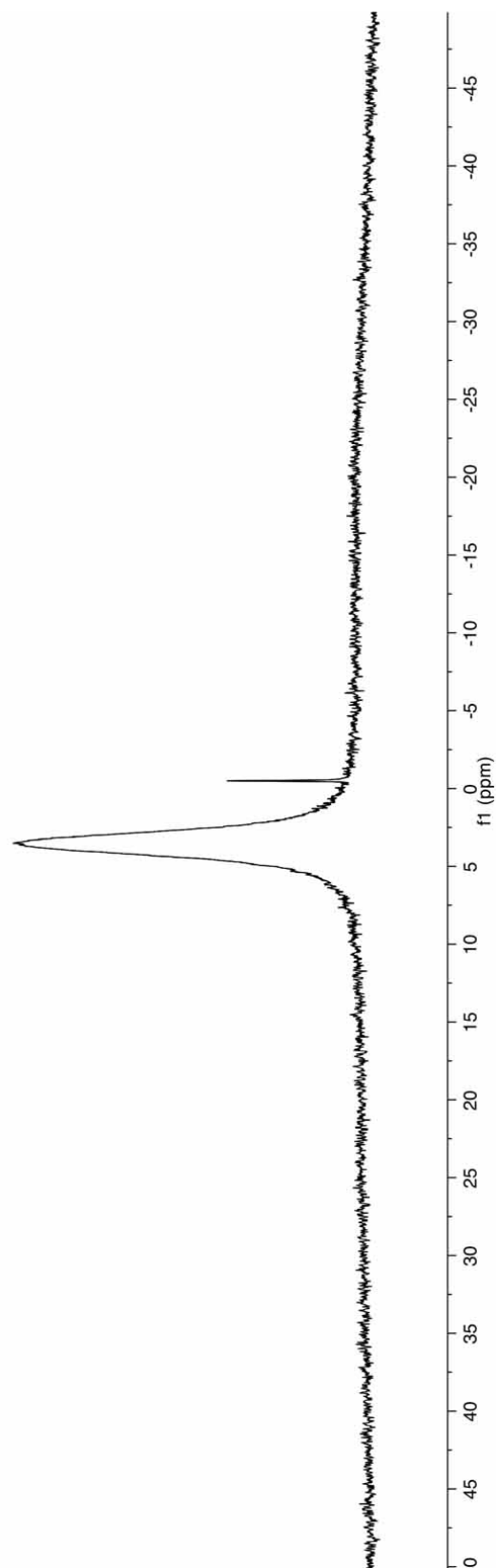
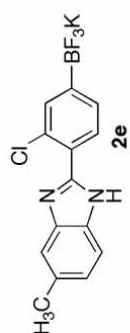
<sup>1</sup>H spectrum (500 MHz, acetone-*d*<sub>6</sub>) of potassium (3-chloro-4-(5-methyl-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**2e**).



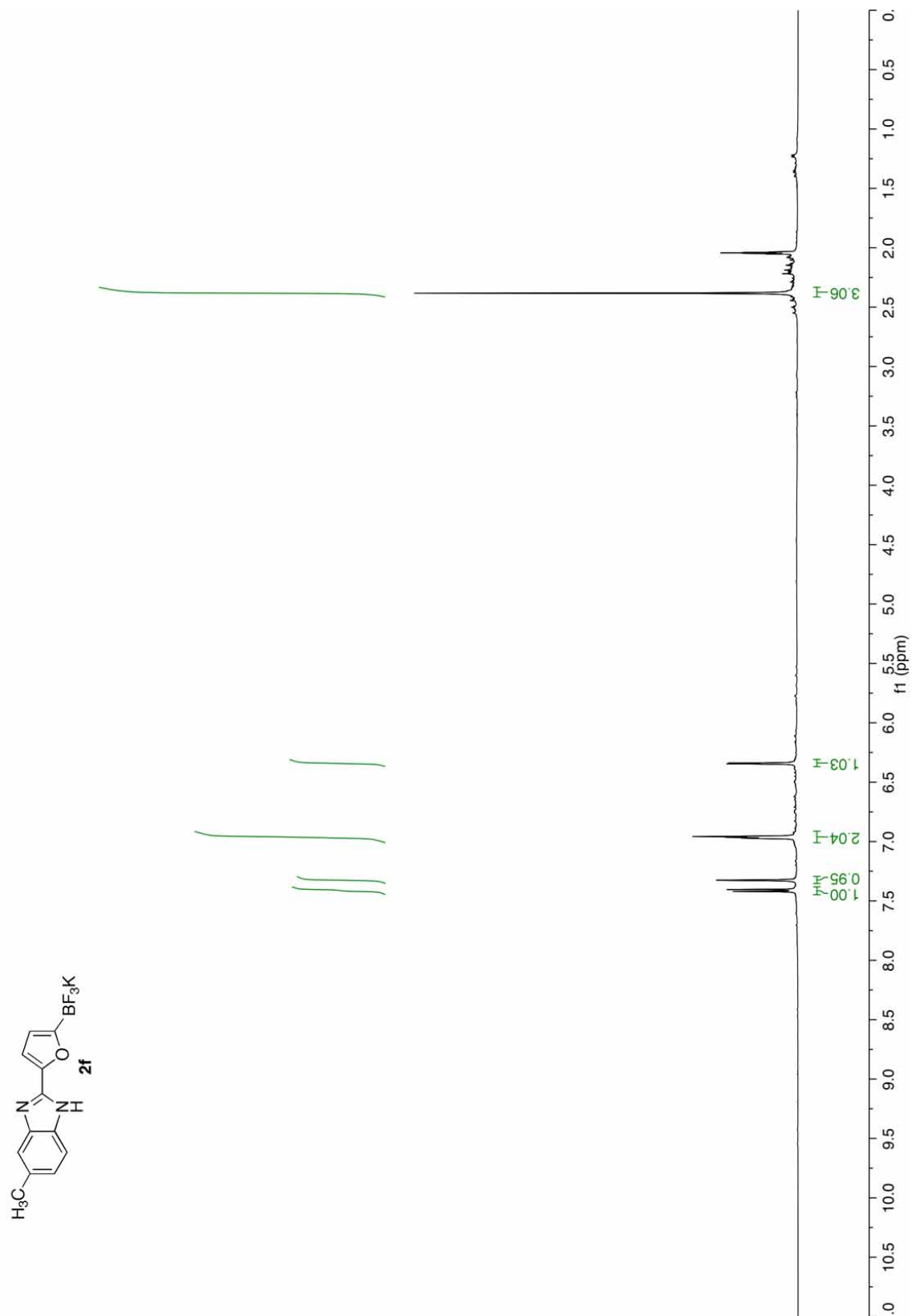
$^{13}\text{C}$  spectrum (125 MHz,  $\text{acetone-}d_6$ ) of potassium (3-Chloro-4-(5-methyl-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**2e**).



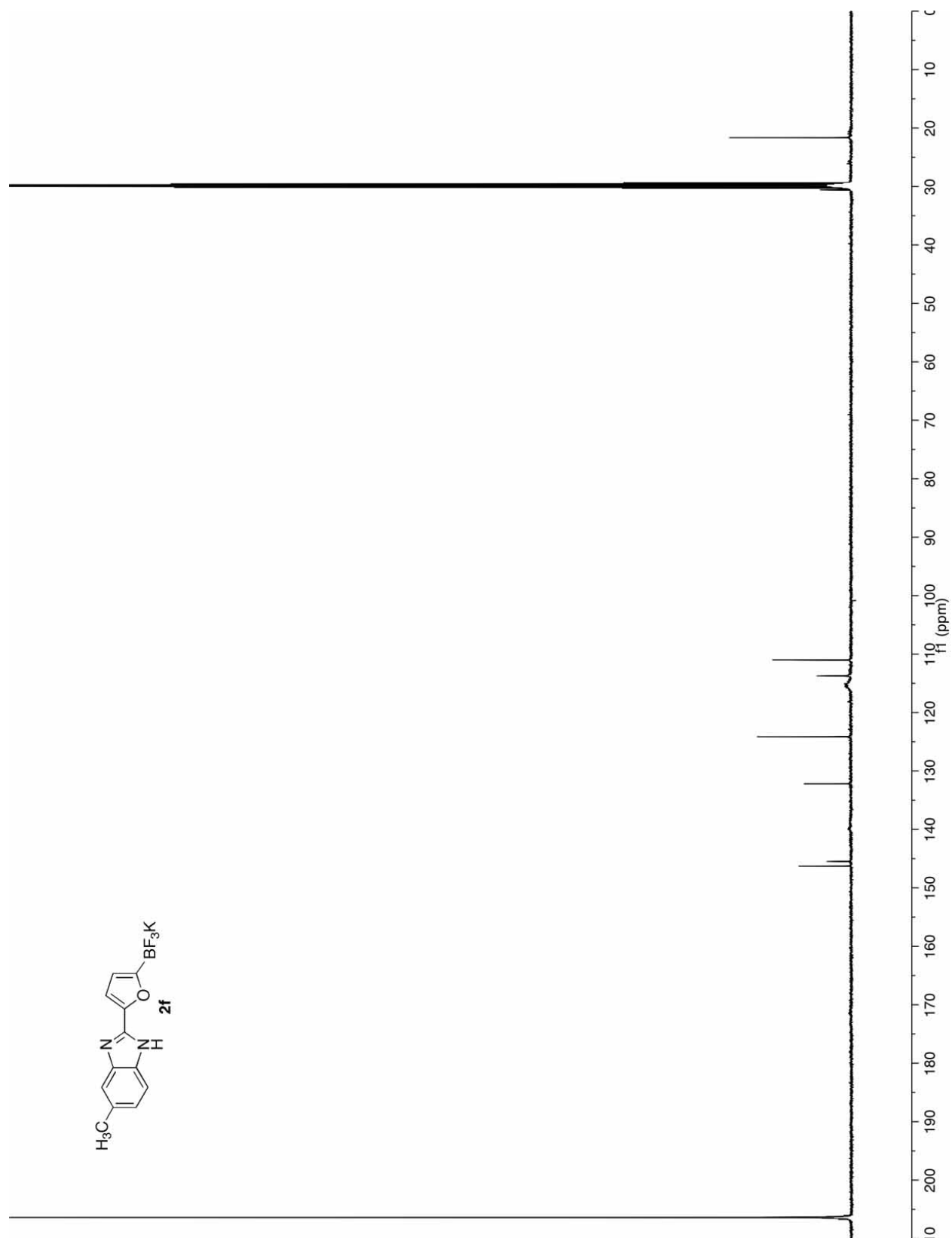
$^{19}\text{F}$  spectrum (470 MHz, acetone- $d_6$ ) of potassium (3-Chloro-4-(5-methyl-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**2e**).

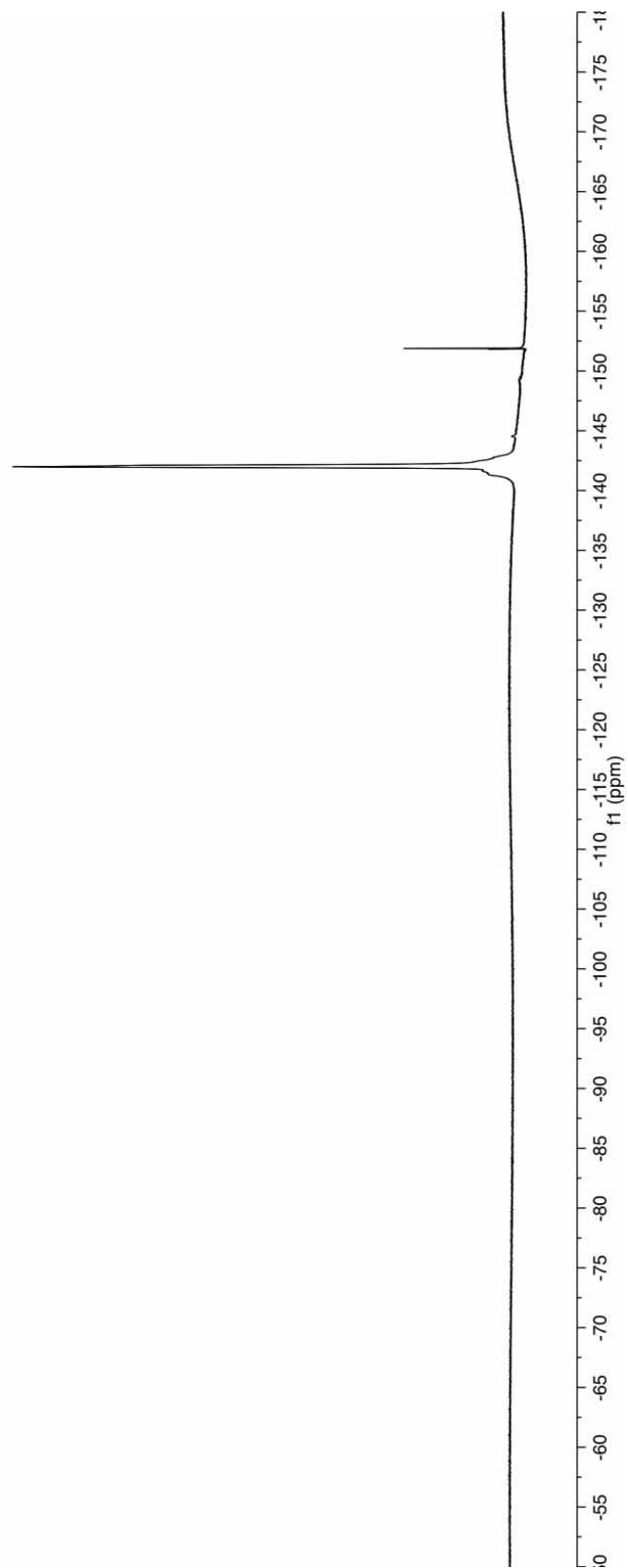
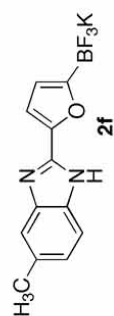


$^{11}\text{B}$  spectrum (128 MHz, acetone- $d_6$ ) of potassium (3-chloro-4-(5-methyl-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**2e**).

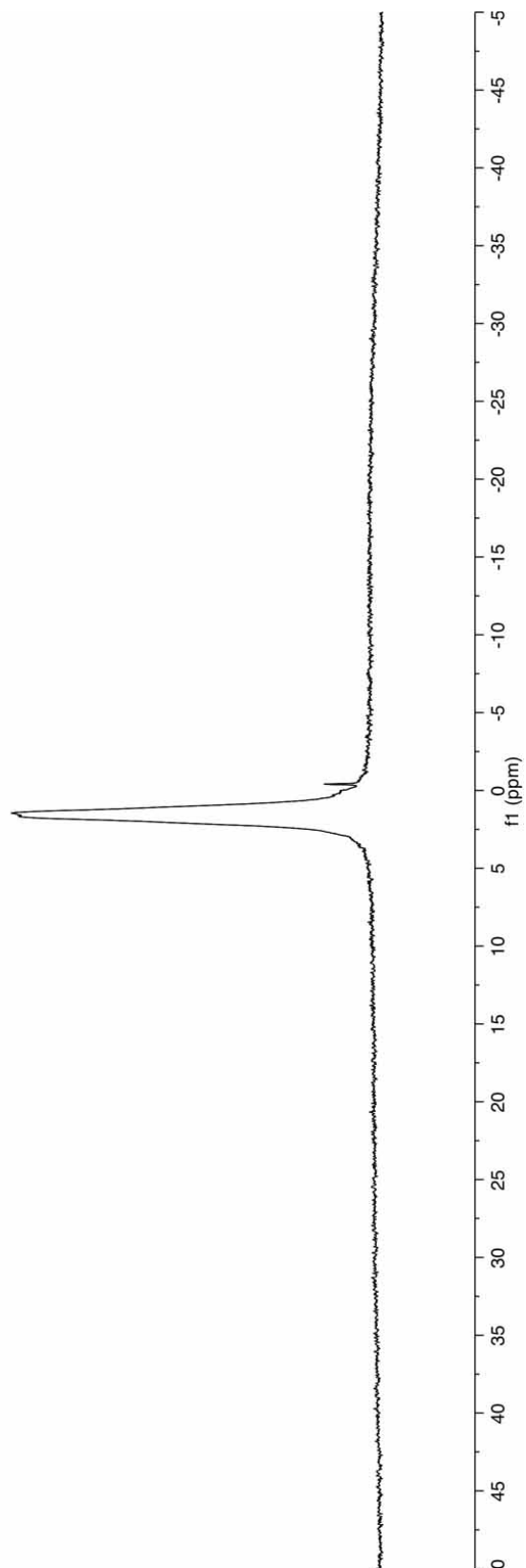
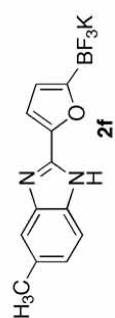


<sup>1</sup>H spectrum (500 MHz, acetone-*d*<sub>6</sub>) of potassium (5-(5-Methyl-1*H*-benzo[*d*]imidazol-2-yl)furan-2-yl)trifluoroborate (**2f**).



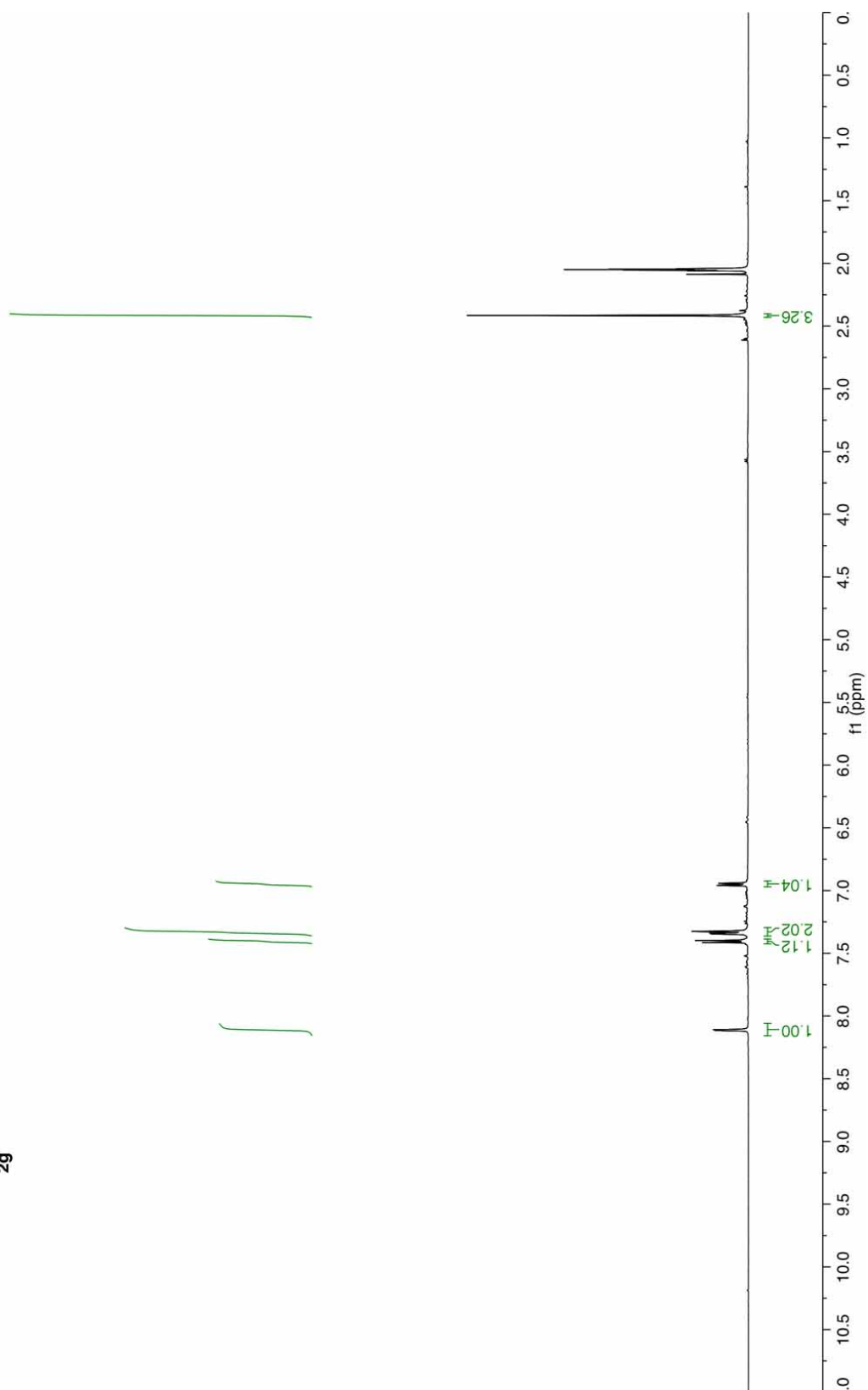
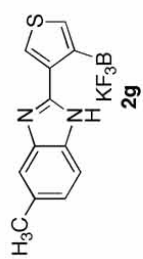


$^{19}\text{F}$  spectrum (470 MHz, acetone- $d_6$ ) of potassium (5-(5-Methyl-1H-benzo[d]imidazol-2-yl)furan-2-yl)trifluoroborate (**2f**).

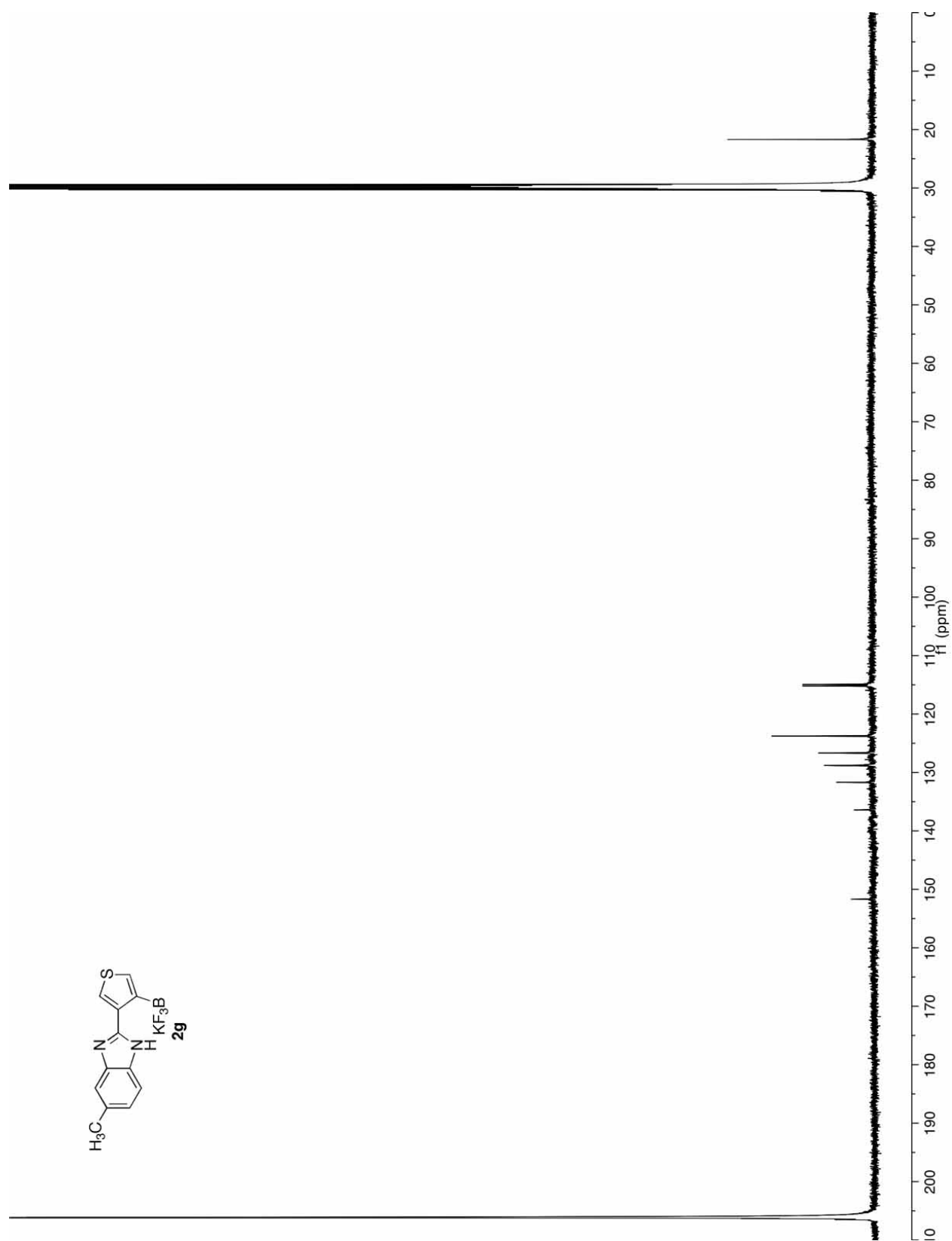


<sup>11</sup>B spectrum (128 MHz, acetone-*d*<sub>6</sub>) of potassium (5-(5-Methyl-1*H*-benzo[*d*]imidazol-2-yl)furan-2-yl)trifluoroborate (**2f**).

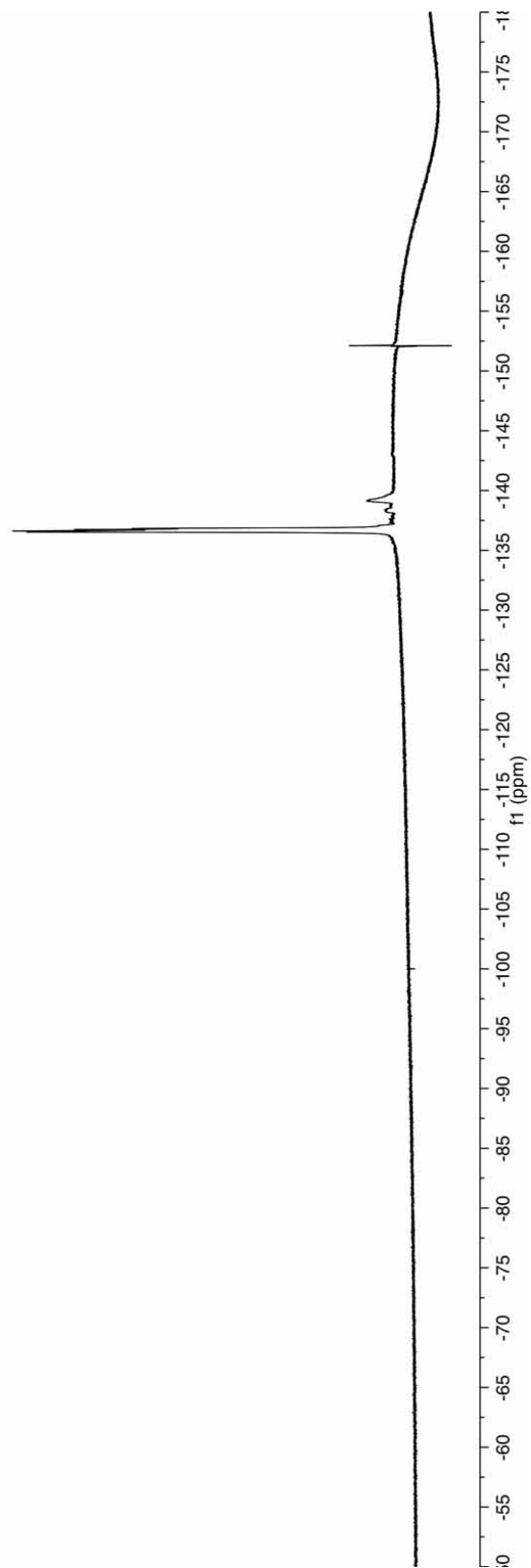
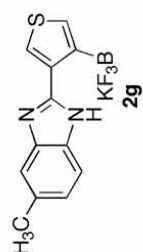




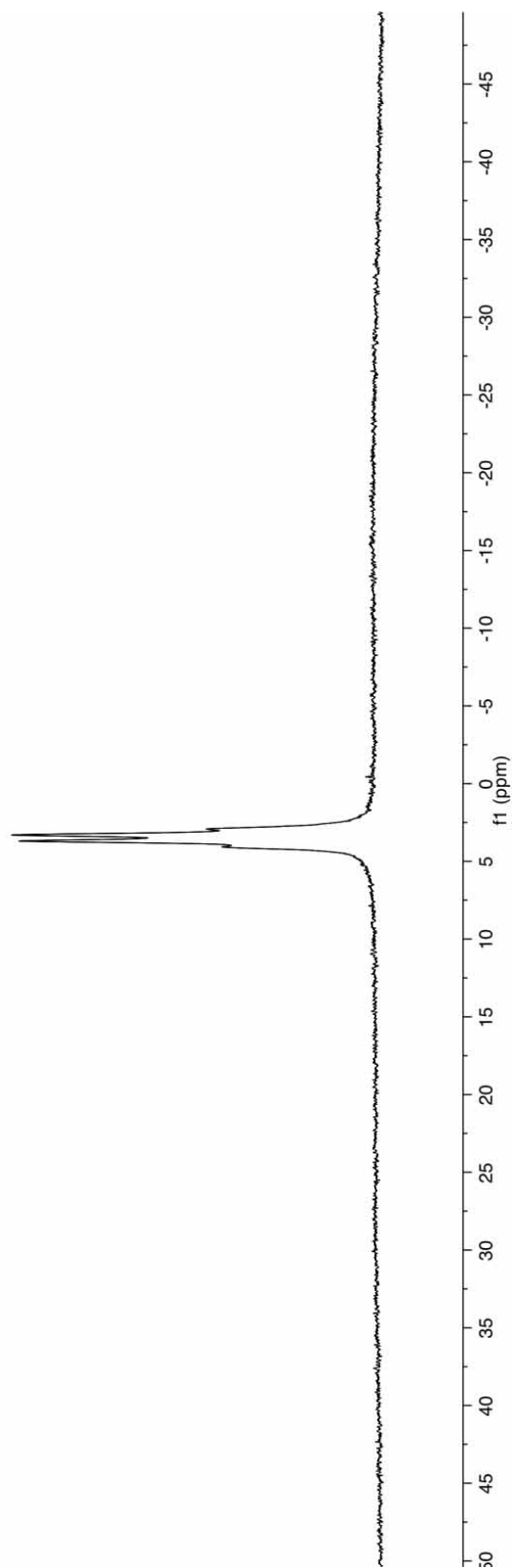
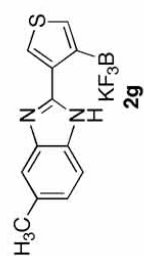
$^1\text{H}$  spectrum (500 MHz, acetone- $d_6$ ) of potassium (4-(5-Methyl-1H-benzo[d]imidazol-2-yl)thiophen-3-yl)trifluoroborate (**2g**).



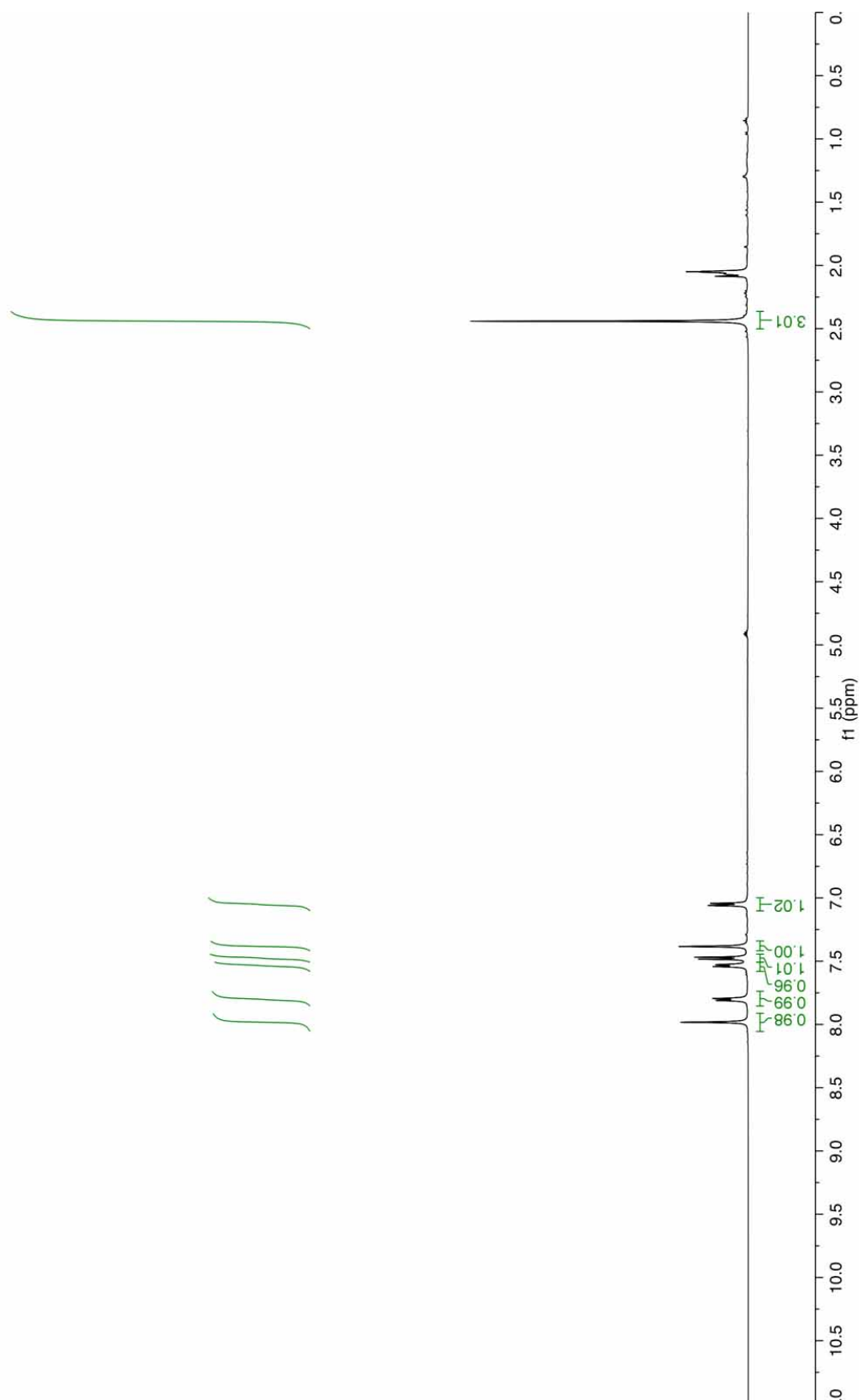
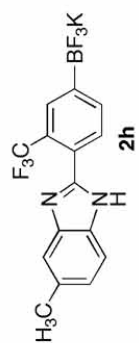
<sup>13</sup>C spectrum (125 MHz, acetone-*d*<sub>6</sub>) of potassium (4-(5-Methyl-1*H*-benzo[*d*]imidazol-2-yl)thiophen-3-yl)trifluoroborate (**2g**).



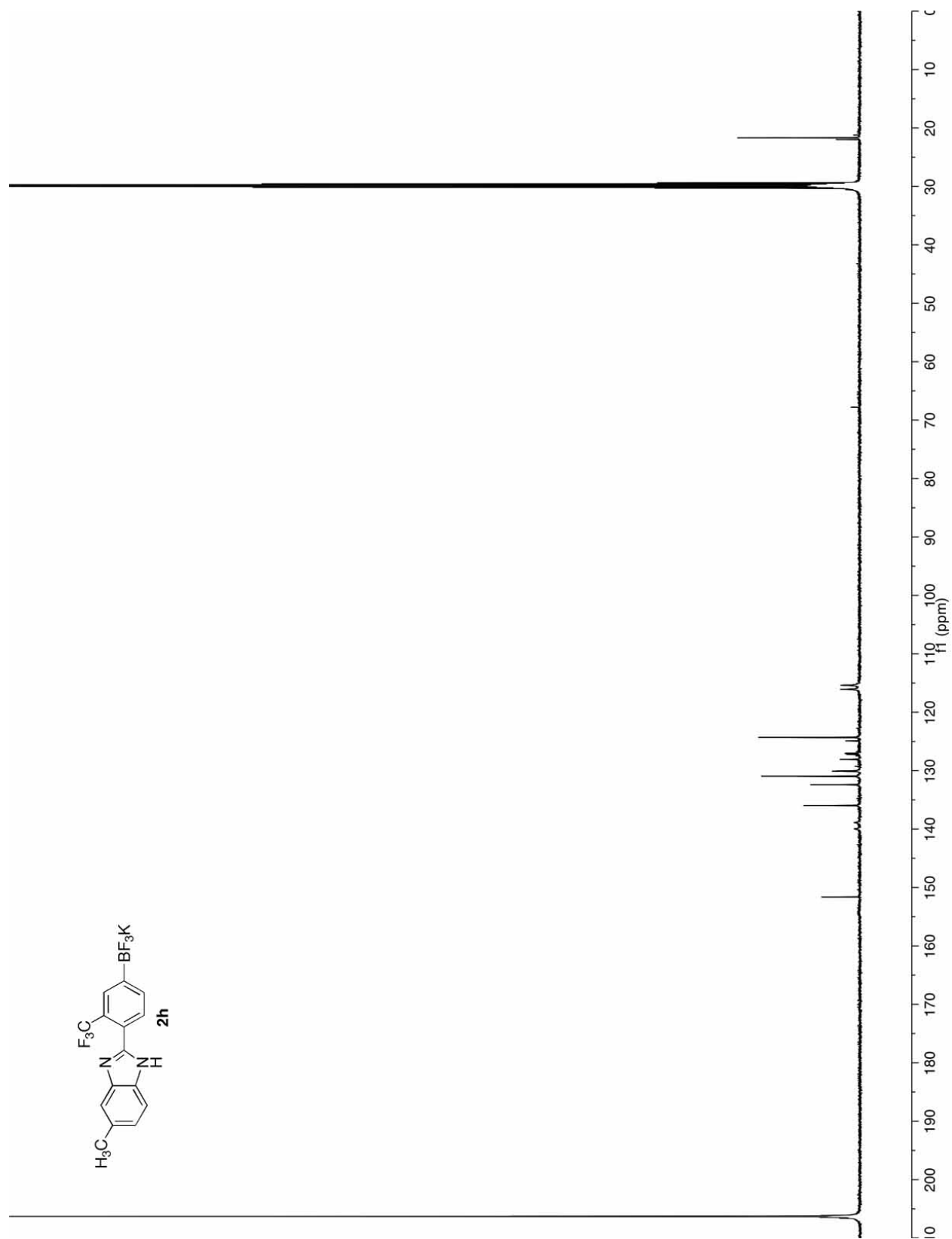
<sup>19</sup>F spectrum (470 MHz, acetone-*d*<sub>6</sub>) of potassium (4-(5-Methyl-1*H*-benzo[*d*]imidazol-2-yl)thiophen-3-yl)trifluoroborate (**2g**).



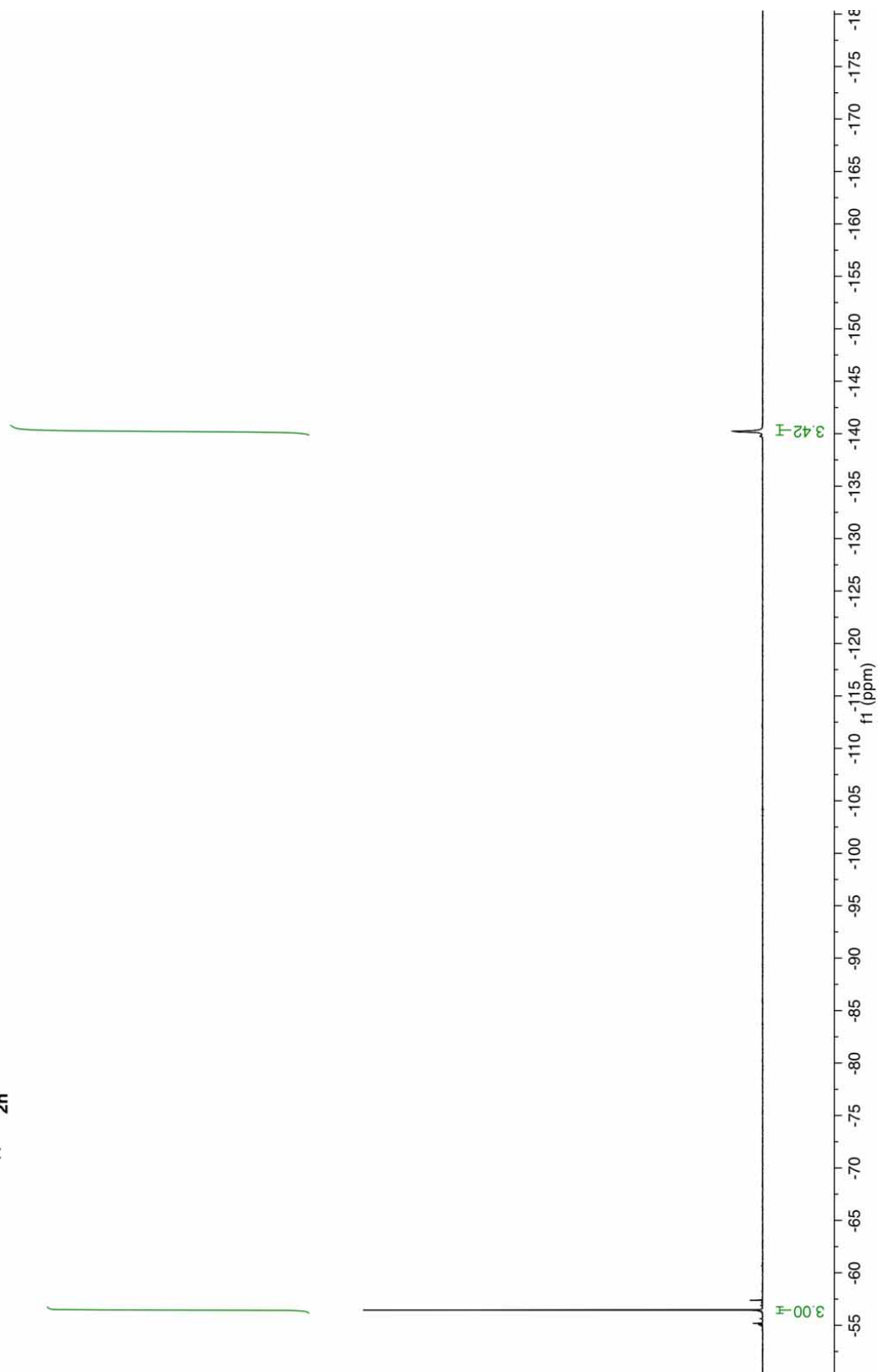
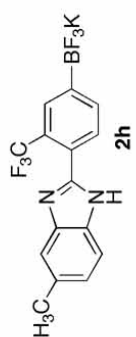
<sup>11</sup>B spectrum (128 MHz, acetone-*d*<sub>6</sub>) of potassium (4-(5-Methyl-1H-benzo[*d*]imidazol-2-yl)thiophen-3-yl)trifluoroborate (**2g**).



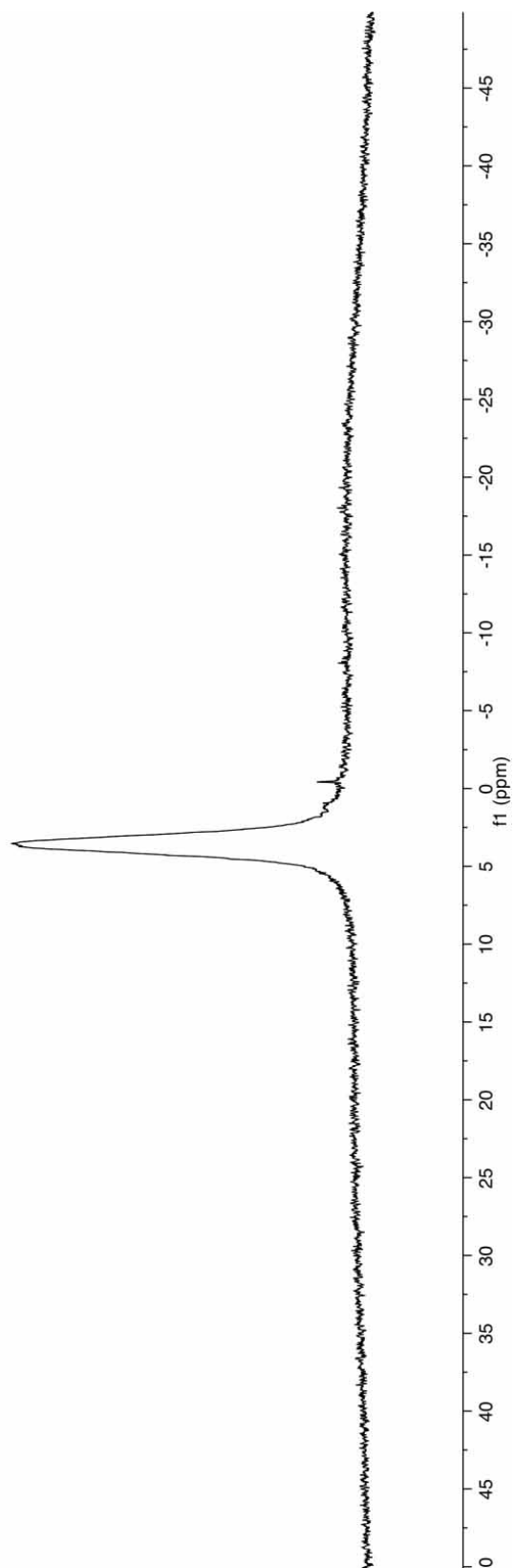
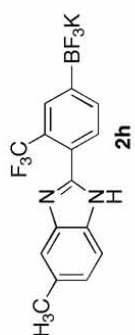
<sup>1</sup>H spectrum (500 MHz, acetone-*d*<sub>6</sub>) of potassium (4-(5-Methyl-1H-benzo[d]imidazol-2-yl)-3-(trifluoromethyl)phenyl)trifluoroborate (**2h**).



$^{13}\text{C}$  spectrum (125 MHz, acetone- $d_6$ ) of potassium (4-(5-Methyl-1H-benzo[d]imidazol-2-yl)-3-(trifluoromethyl)phenyl)trifluoroborate (**2h**).

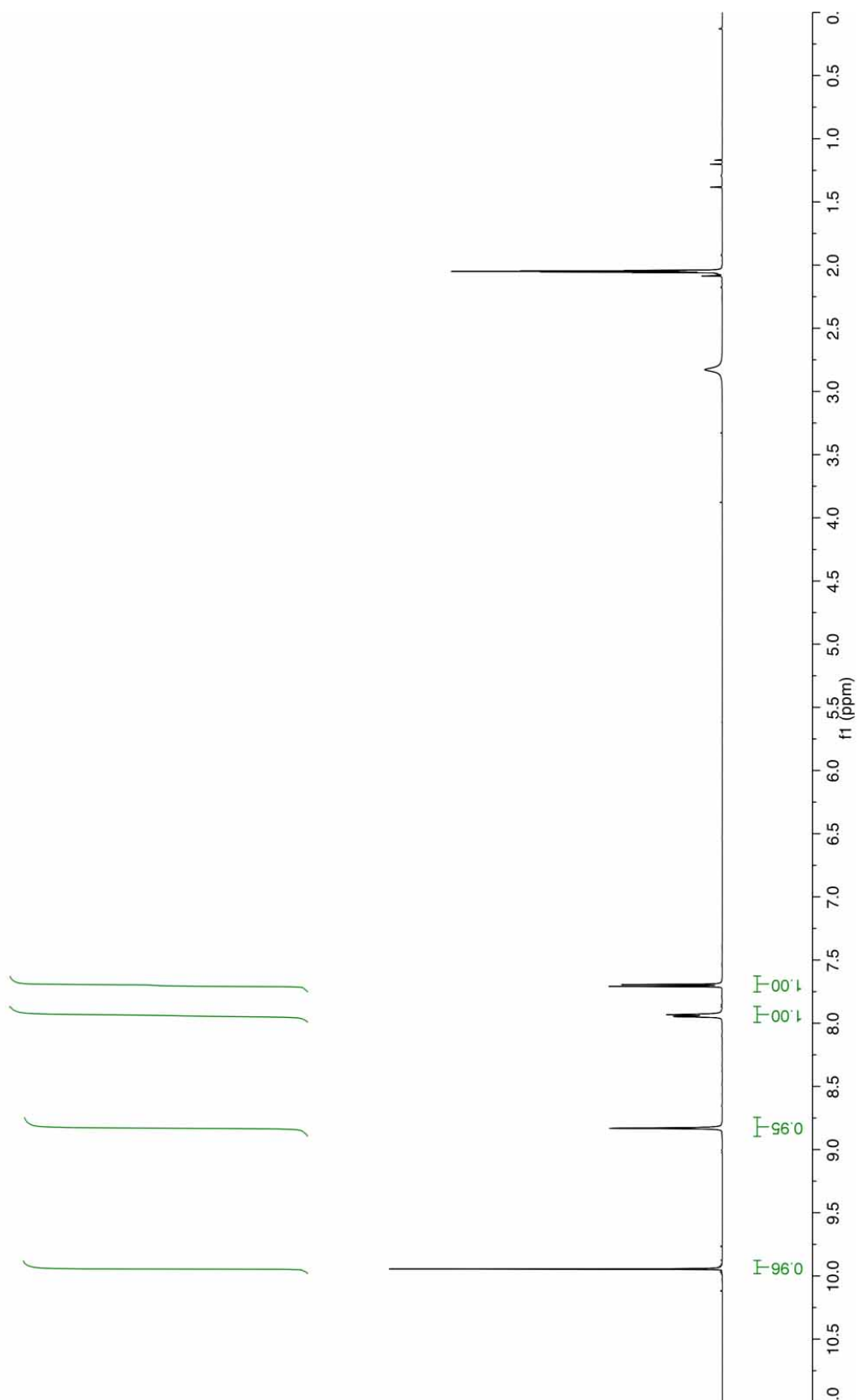
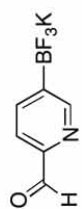


$^{19}\text{F}$  spectrum (470 MHz, acetone- $d_6$ ) of potassium (4-(5-Methyl-1H-benzo[d]imidazol-2-yl)-3-(trifluoromethyl)phenyl)trifluoroborate (**2h**).

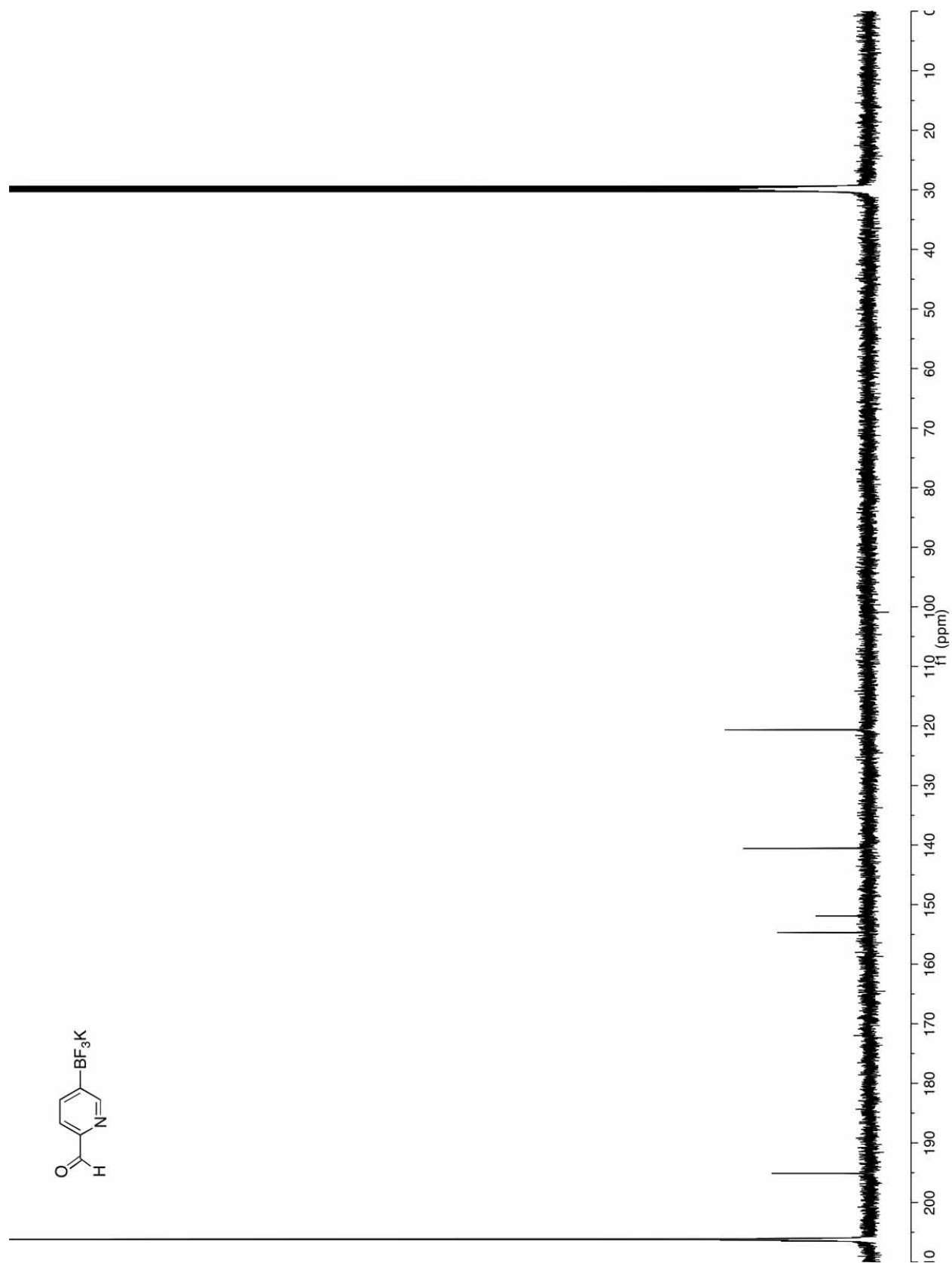


$^{11}\text{B}$  spectrum (128 MHz, acetone- $d_6$ ) of potassium (4-(5-Methyl-1H-benzo[d]imidazol-2-yl)-3-(trifluoromethyl)phenyl)trifluoroborate (**2h**).

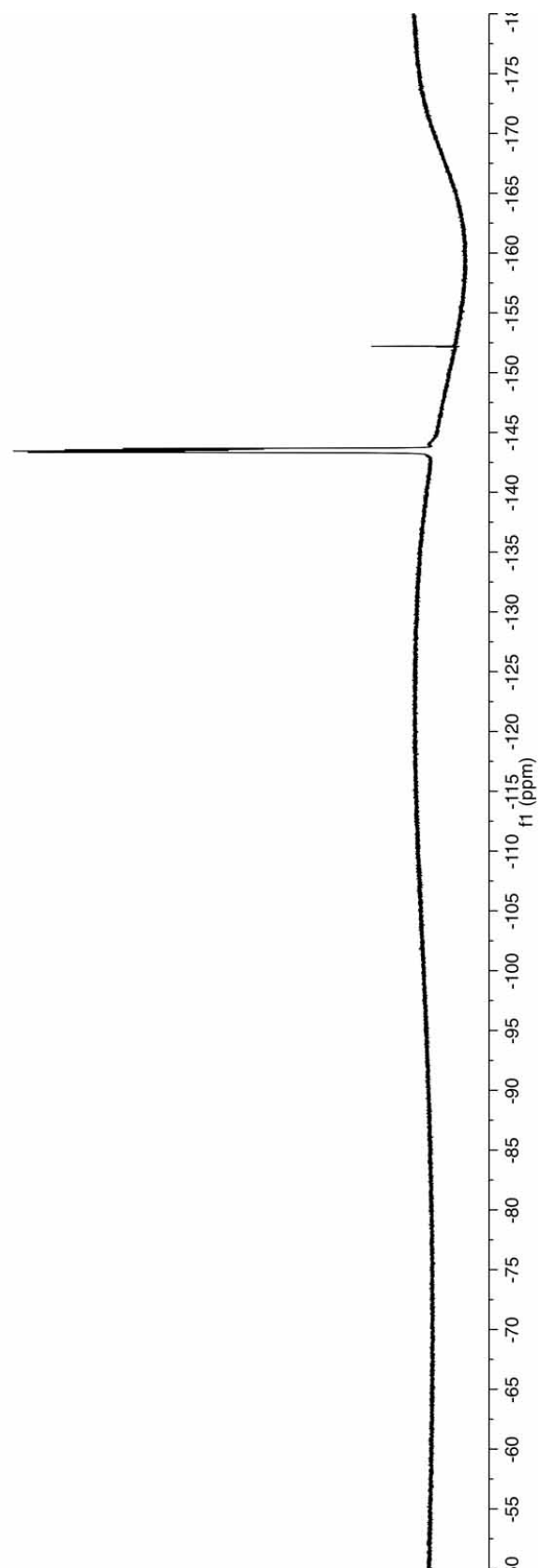
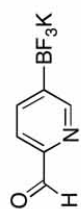




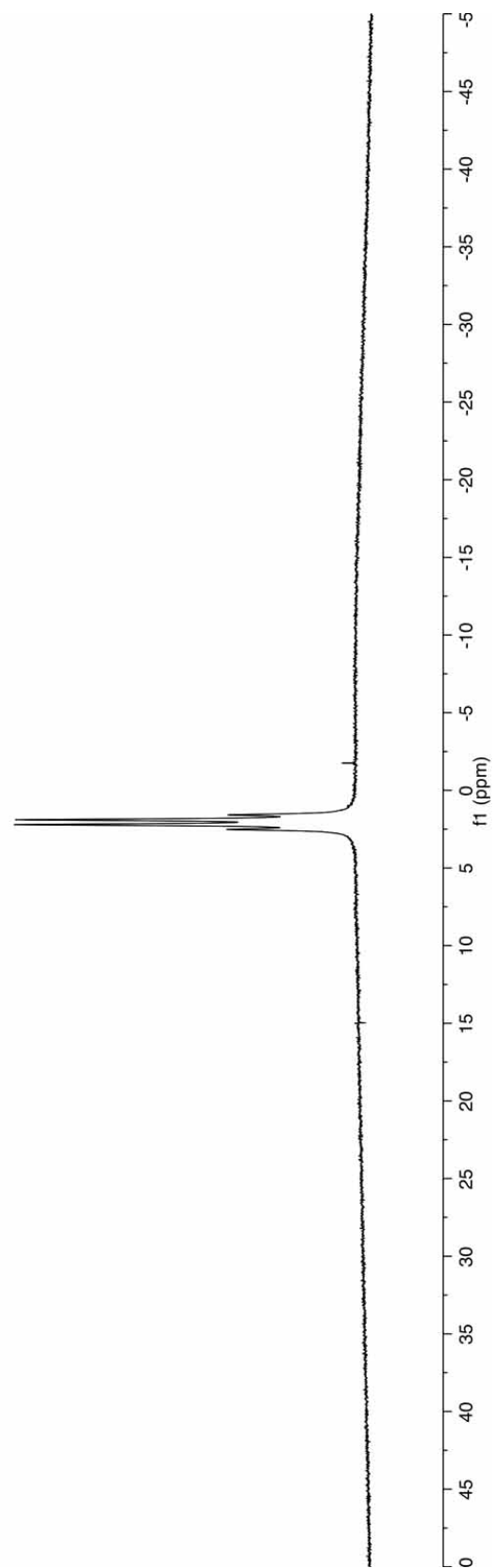
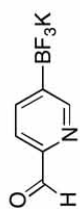
<sup>1</sup>H spectrum (500 MHz, acetone-*d*<sub>6</sub>) of potassium (6-formylpyridin-3-yl)trifluoroborate



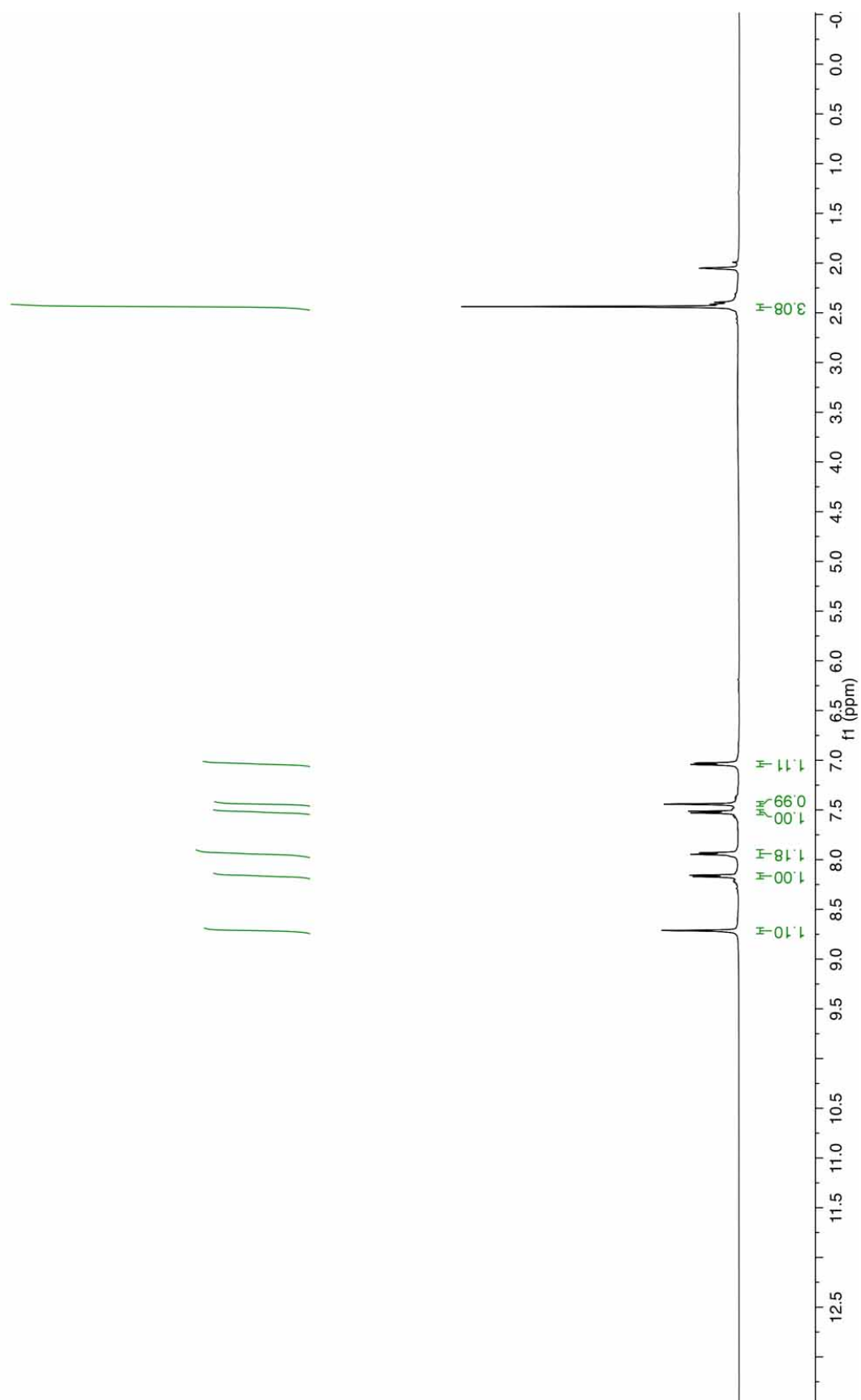
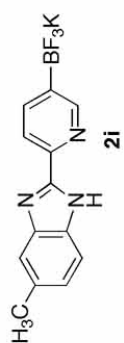
$^{13}\text{C}$  spectrum (125 MHz, acetone- $d_6$ ) of potassium (6-formylpyridin-3-yl)trifluoroborate



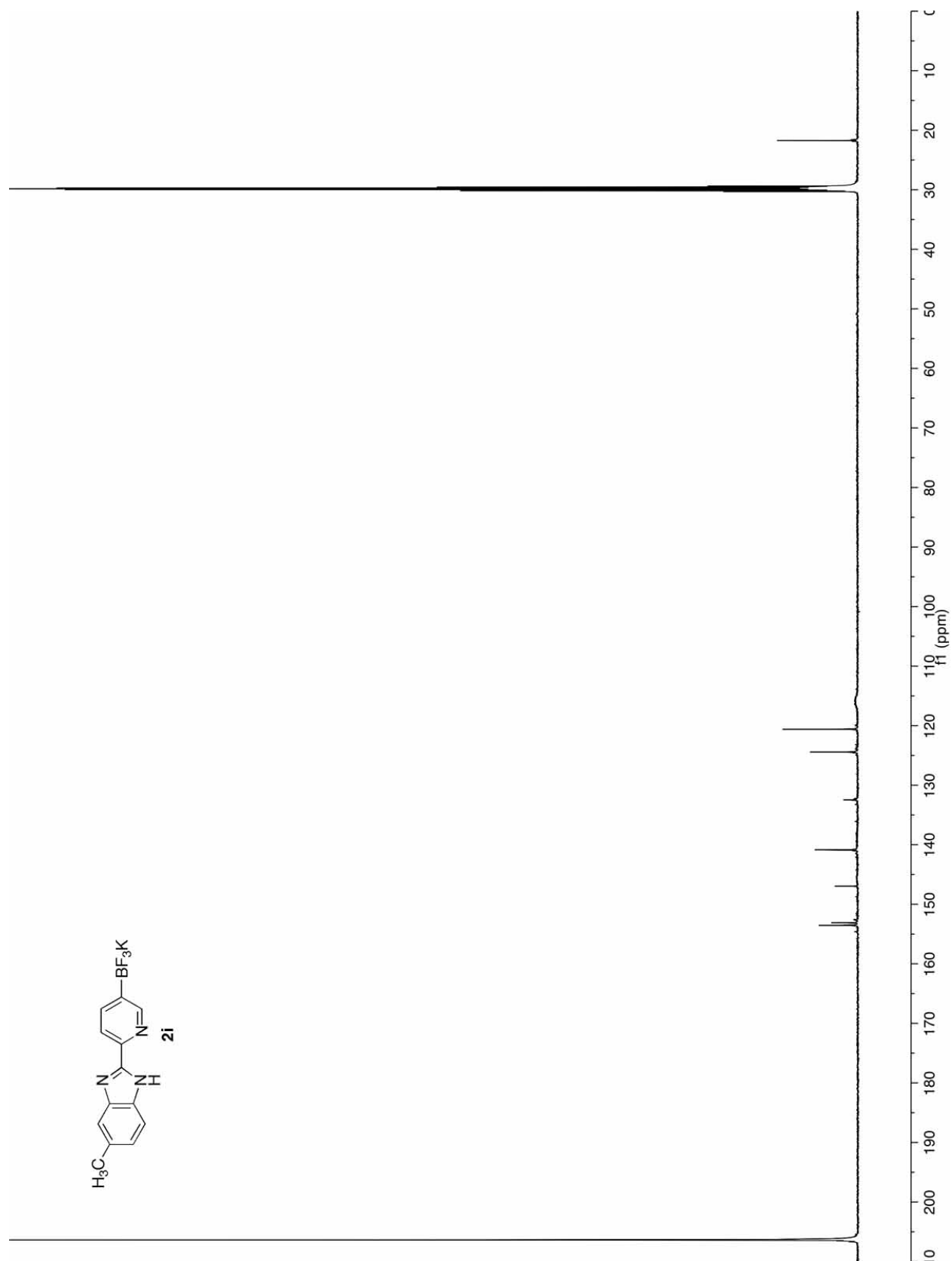
$^{19}\text{F}$  spectrum (470 MHz, acetone- $d_6$ ) of potassium (6-formylpyridin-3-yl)trifluoroborate



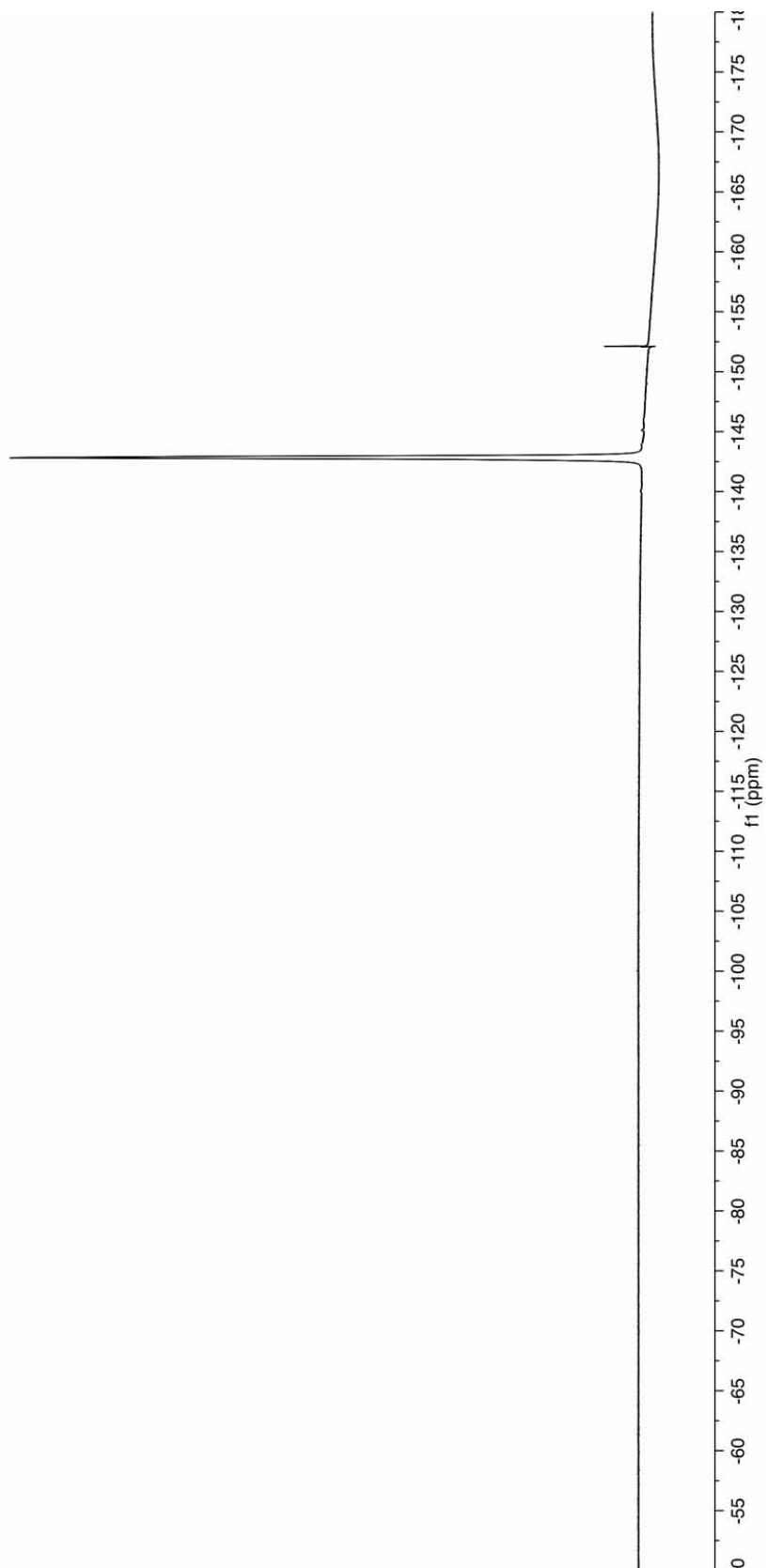
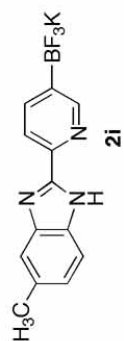
$^{11}\text{B}$  spectrum (128 MHz, acetone- $d_6$ ) of potassium (6-formylpyridin-3-yl)trifluoroborate



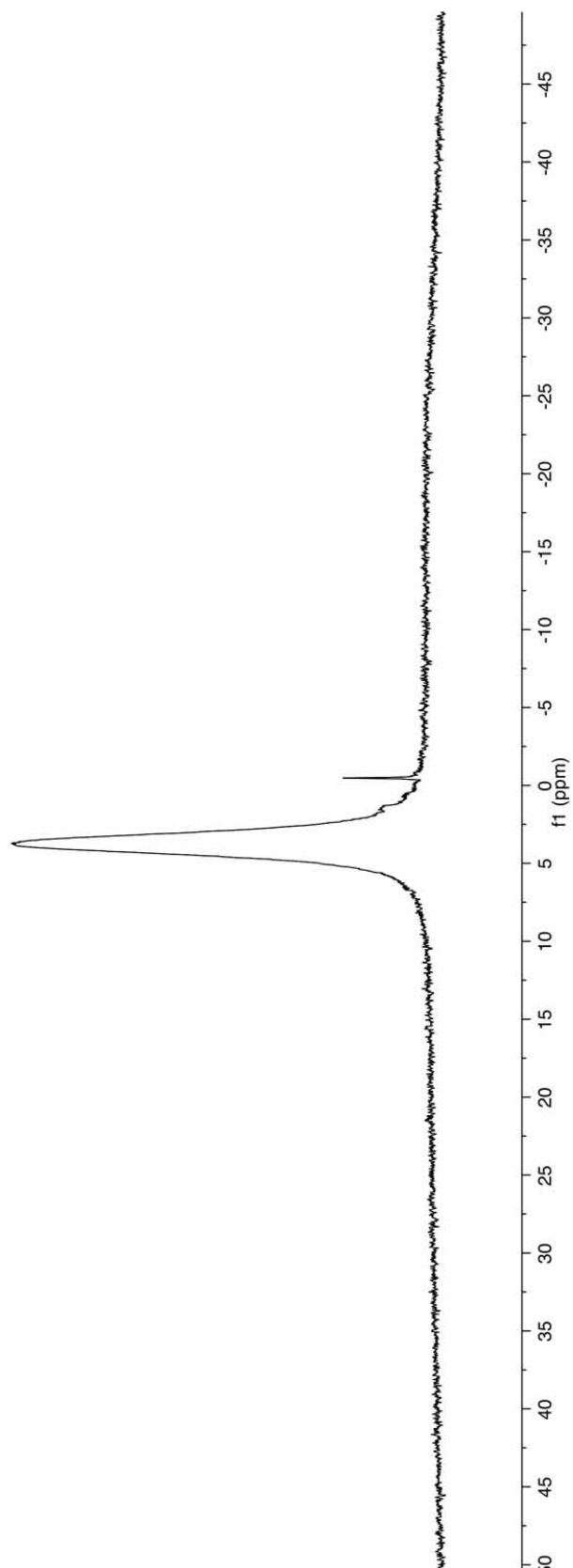
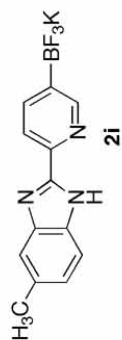
$^1\text{H}$  spectrum (500 MHz, acetone- $d_6$ ) of potassium (6-(5-Methyl-1*H*-benzo[*d*]imidazol-2-yl)pyridin-3-yl)trifluoroborate (**2i**).



$^{13}\text{C}$  spectrum (125 MHz, acetone- $d_6$ ) of potassium (6-(5-Methyl-1*H*-benzo[*d*]imidazol-2-yl)pyridin-3-yl)trifluoroborate (**2i**).

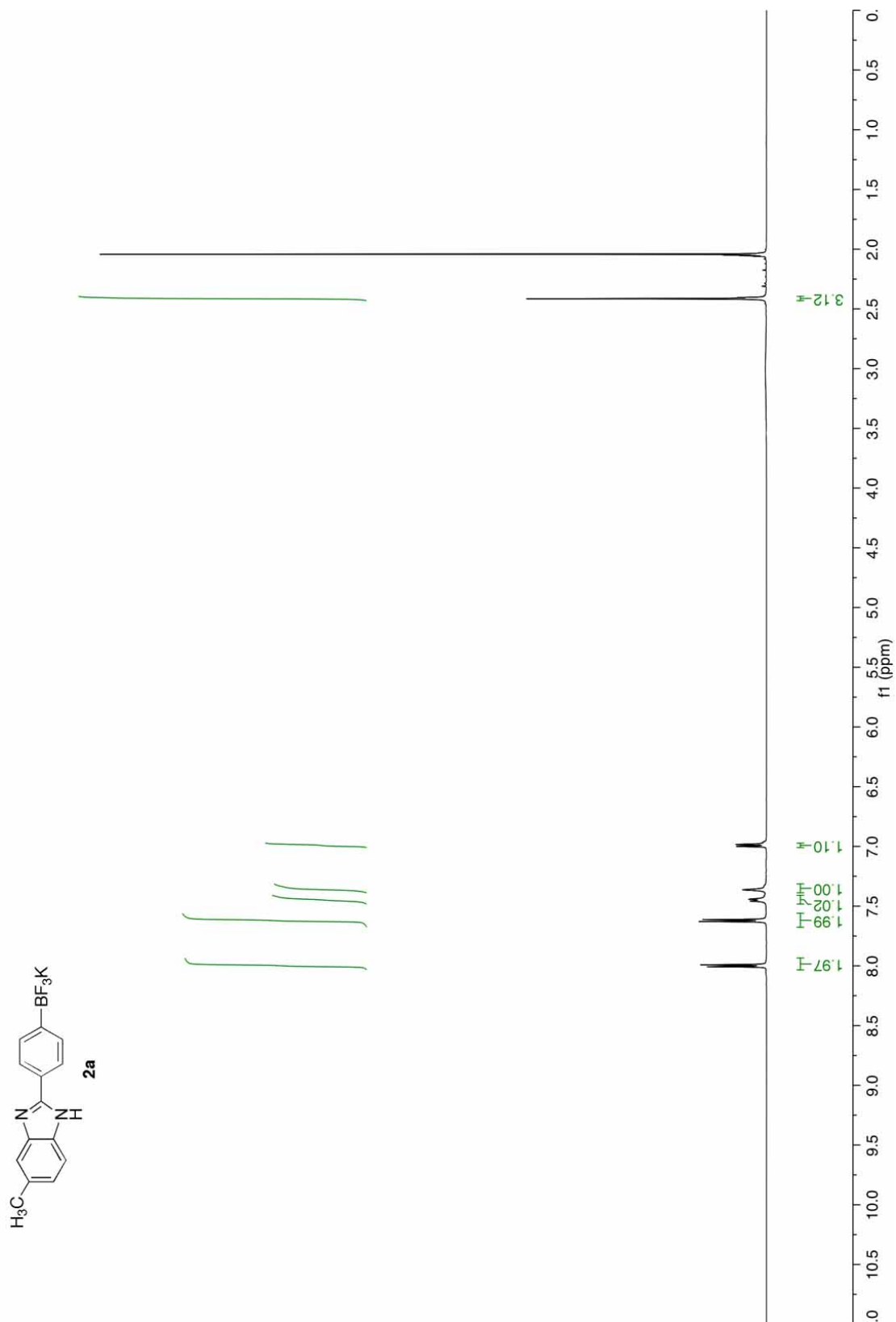


$^{19}\text{F}$  spectrum (470 MHz, acetone- $d_6$ ) of potassium (6-(5-Methyl-1H-benzo[d]imidazol-2-yl)pyridin-3-yl)trifluoroborate (**2i**).

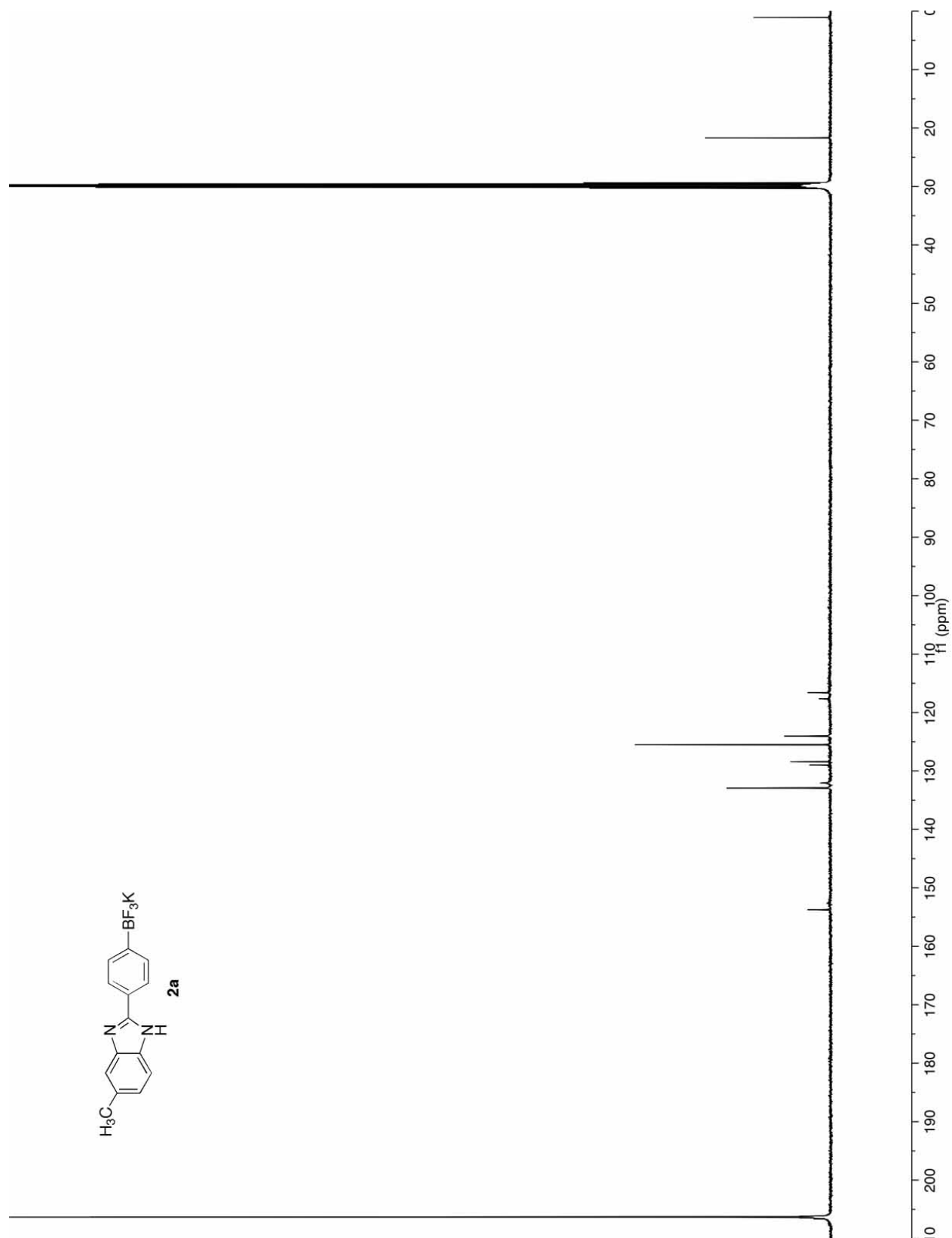


$^{11}\text{B}$  spectrum (128 MHz, acetone- $d_6$ ) of potassium (6-(5-Methyl-1*H*-benzo[*d*]imidazol-2-yl)pyridin-3-yl)trifluoroborate (**2i**).

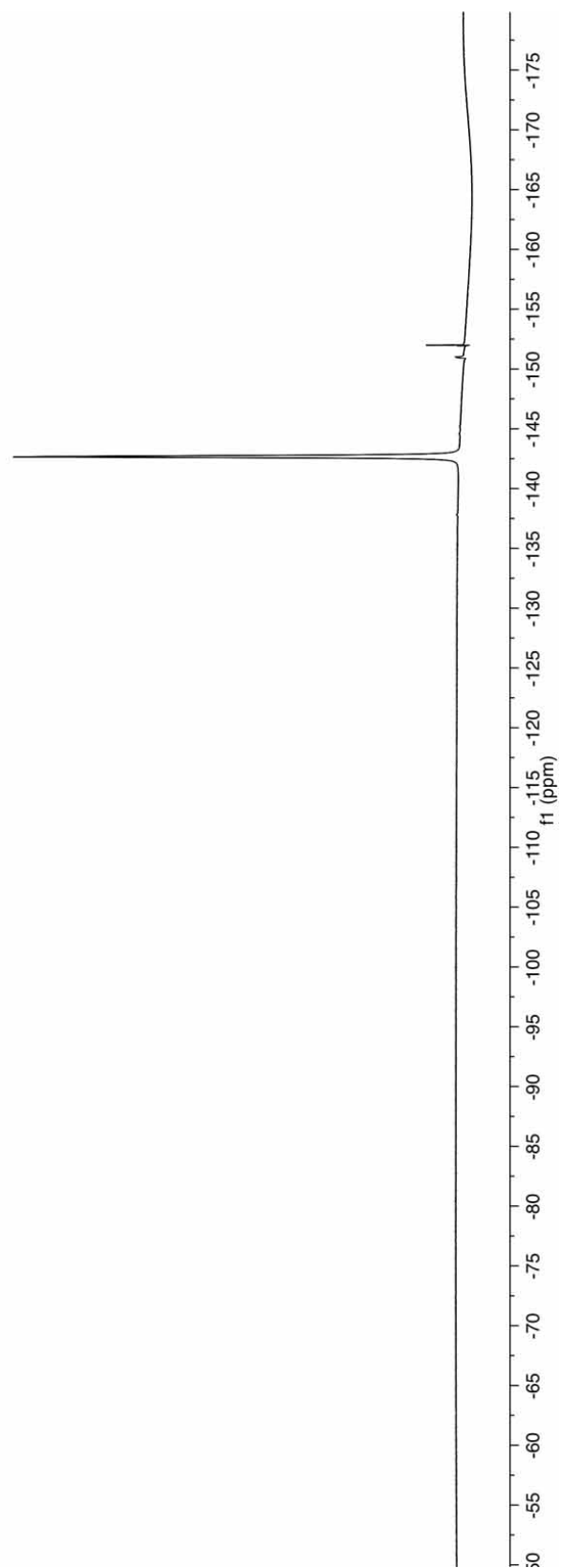
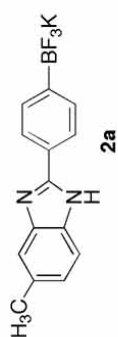




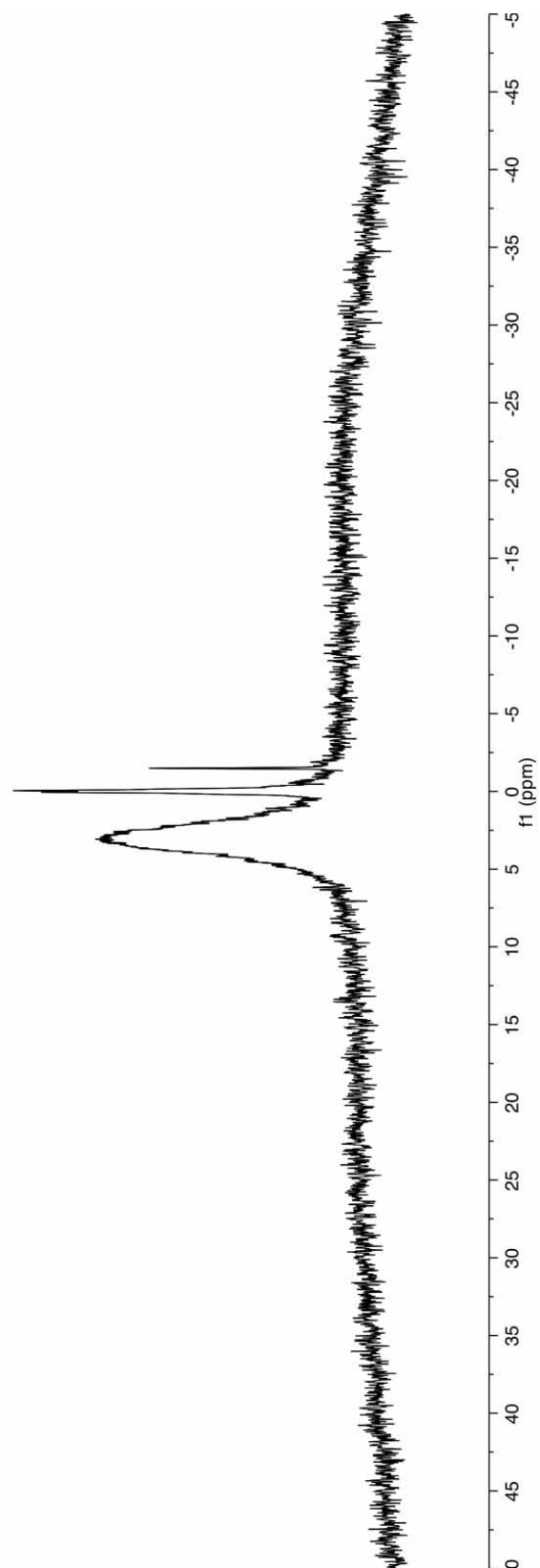
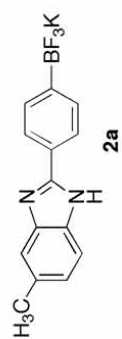
<sup>1</sup>H spectrum (500 MHz, acetone-*d*<sub>6</sub>) of potassium (4-(5-Methyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl)trifluoroborate (**2a**).



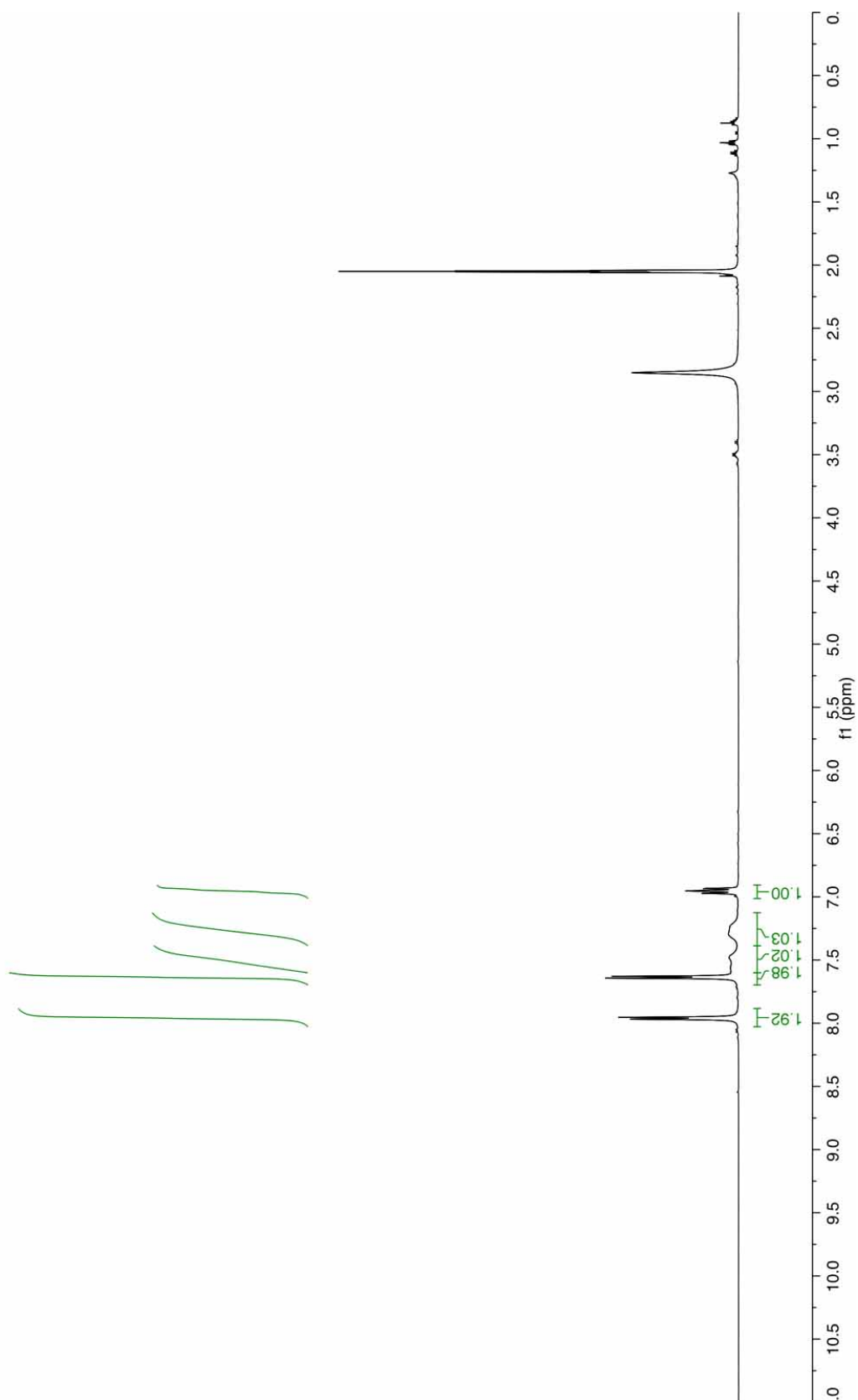
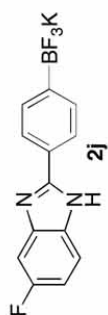
$^{13}\text{C}$  spectrum (125 MHz, acetone- $d_6$ ) of potassium 2(4-(5-Methyl-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**2a**).



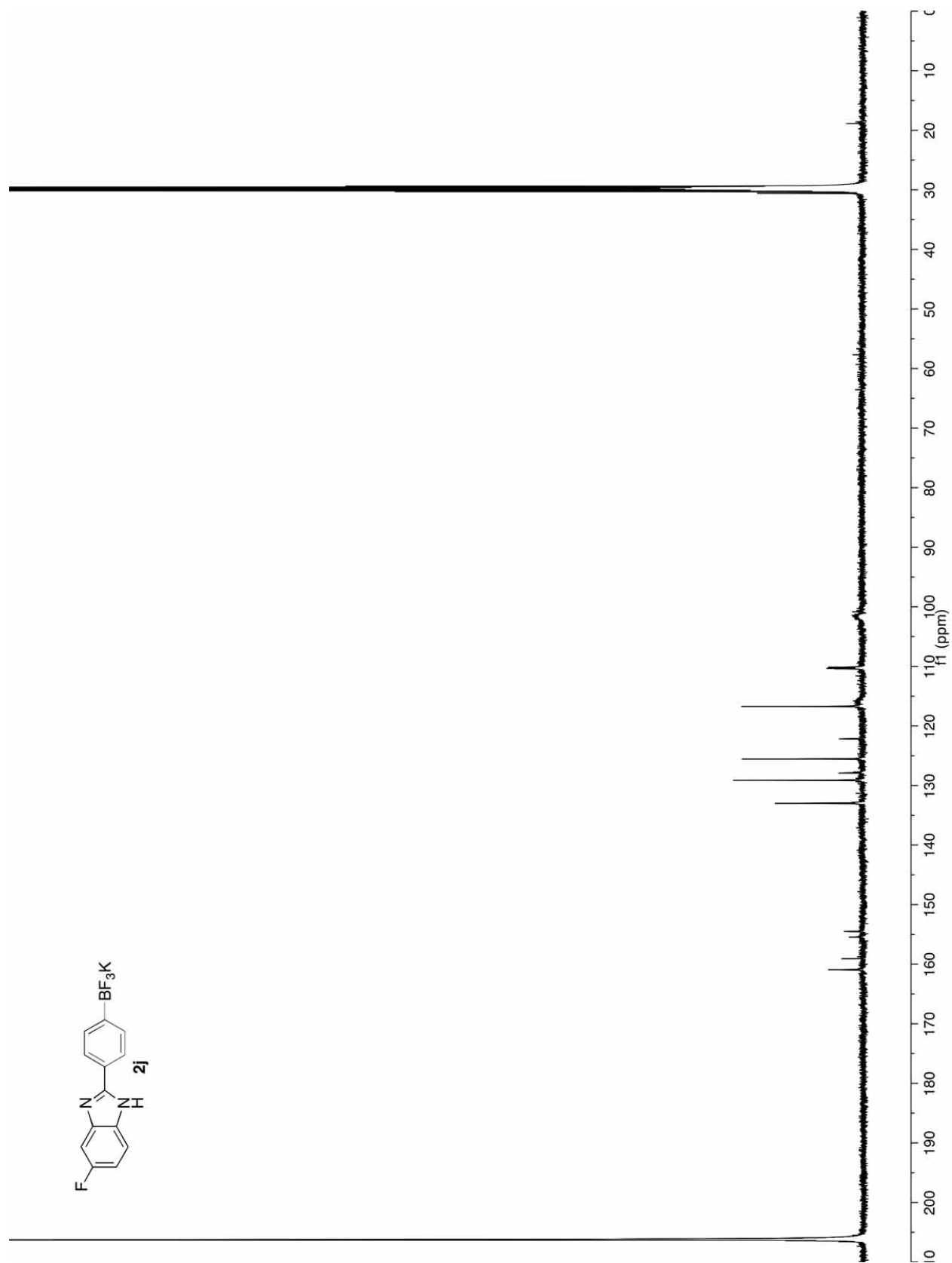
$^{19}\text{F}$  spectrum (470 MHz, acetone- $d_6$ ) of potassium (4-(5-Methyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl)trifluoroborate (**2a**).



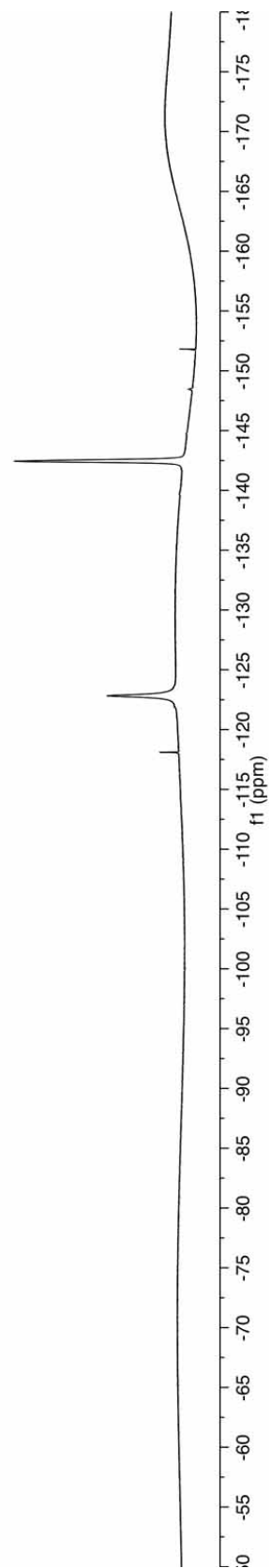
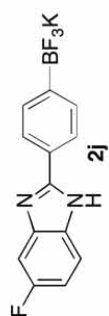
$^{11}\text{B}$  spectrum (128 MHz, acetone- $d_6$ ) of potassium (4-(5-Methyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl)trifluoroborate (**2a**).



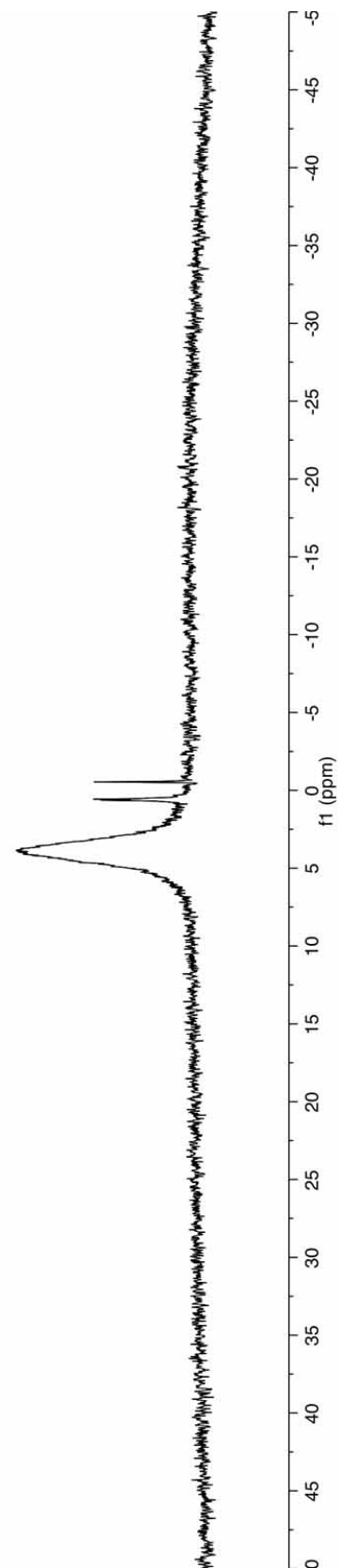
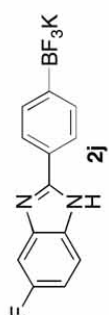
<sup>1</sup>H spectrum (500 MHz, acetone-*d*<sub>6</sub>) of potassium (4-(5-Fluoro-1H-benzo[*d*]imidazol-2-yl)phenyl)trifluoroborate (**2j**).



$^{13}\text{C}$  spectrum (125 MHz, acetone- $d_6$ ) of potassium (4-(5-Fluoro-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**2j**).

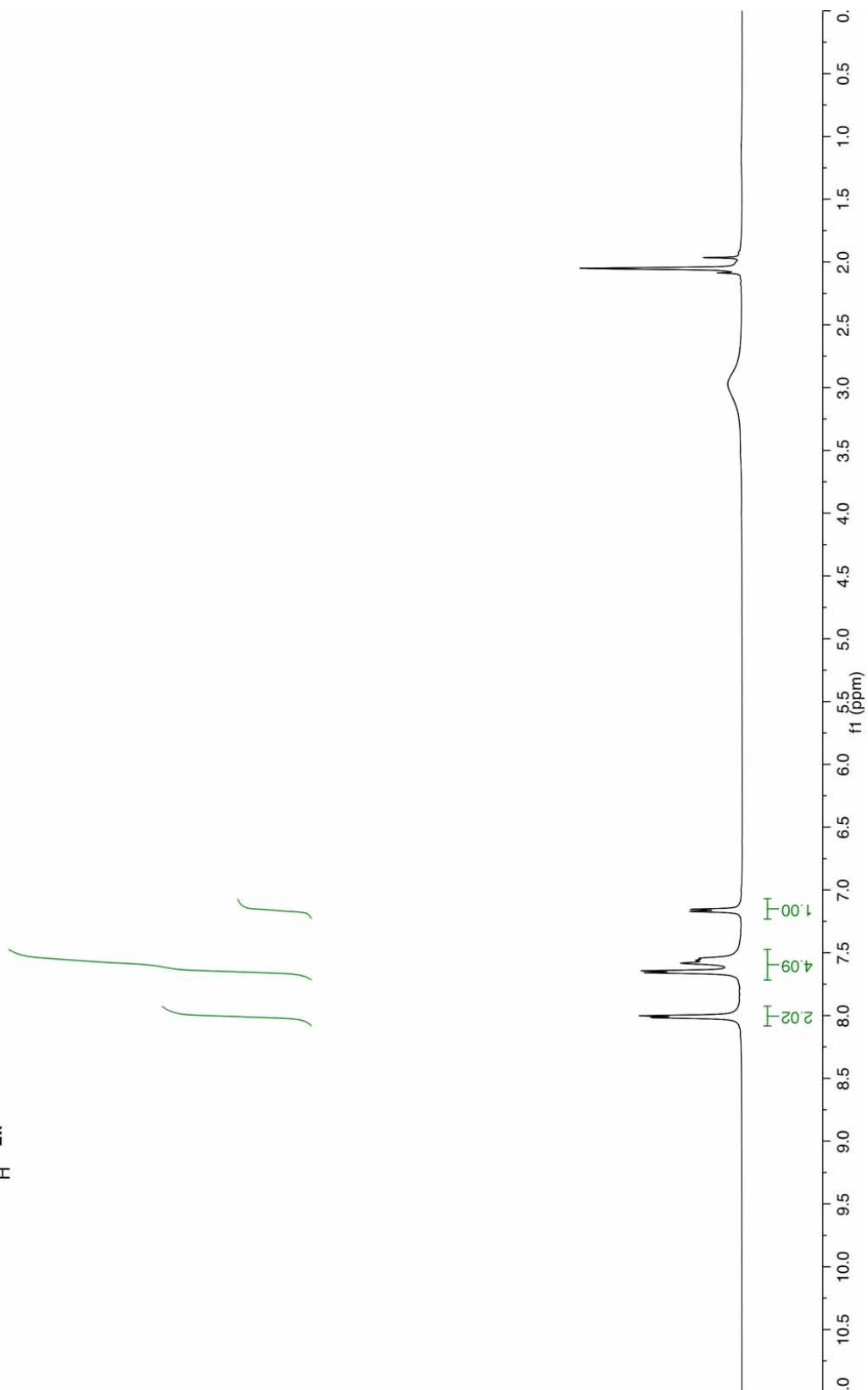
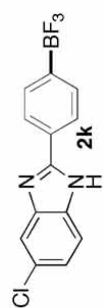


$^{19}\text{F}$  spectrum (470 MHz, acetone- $d_6$ ) of potassium (4-(5-Fluoro-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**2j**).

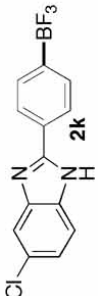


$^{11}\text{B}$  spectrum (128 MHz, acetone- $d_6$ ) of potassium (4-(5-fluoro-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**2j**).

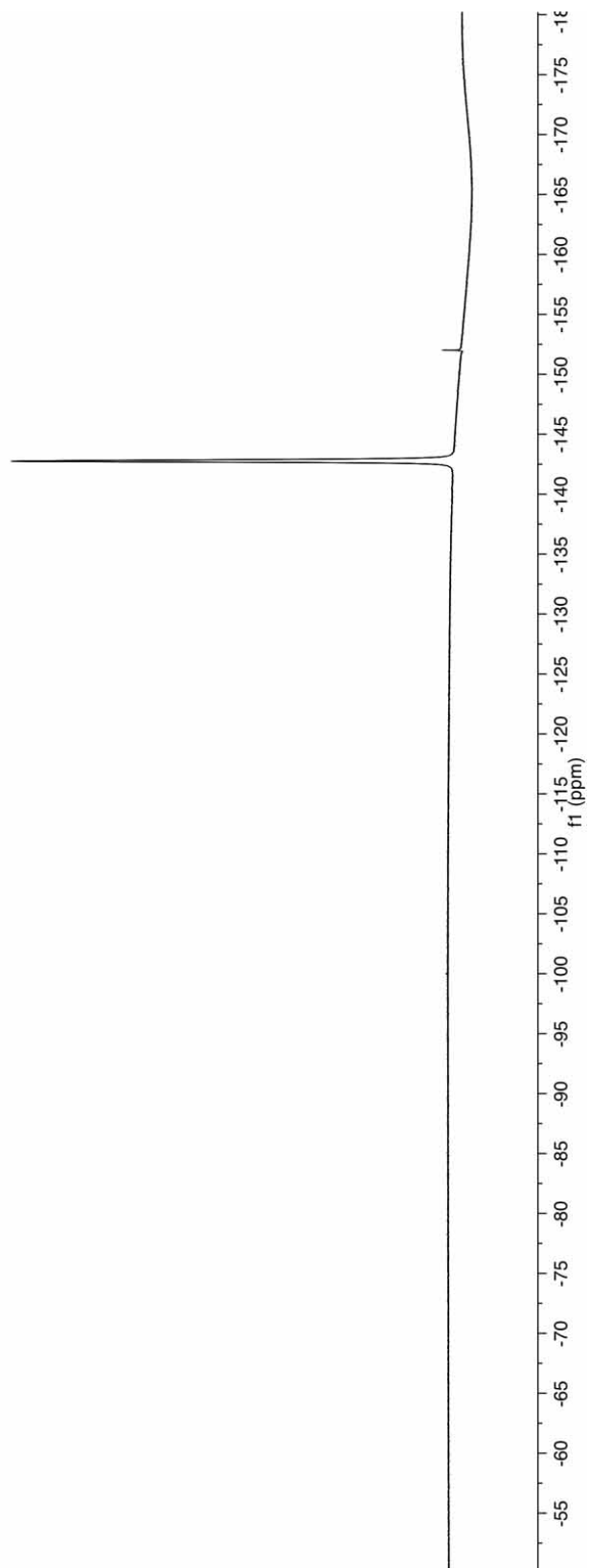
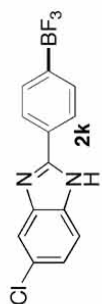




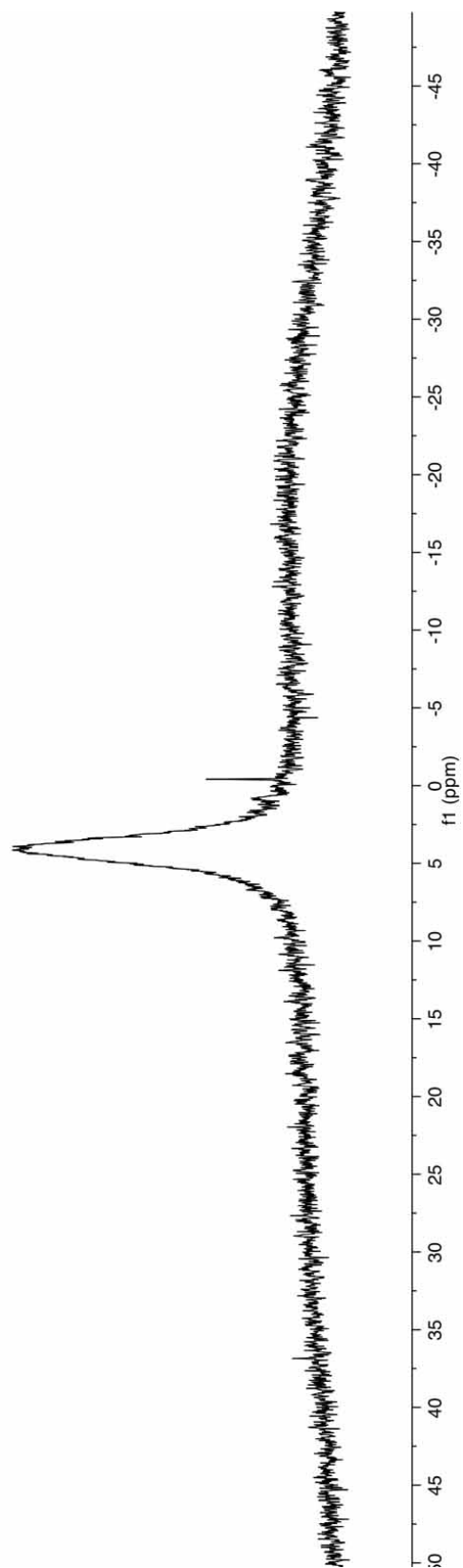
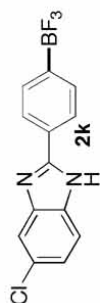
$^1\text{H}$  spectrum (500 MHz, acetone- $d_6$ ) of potassium (4-(5-chloro-1H-benzimidazol-2-yl)phenyl)trifluoroborate (**2k**).



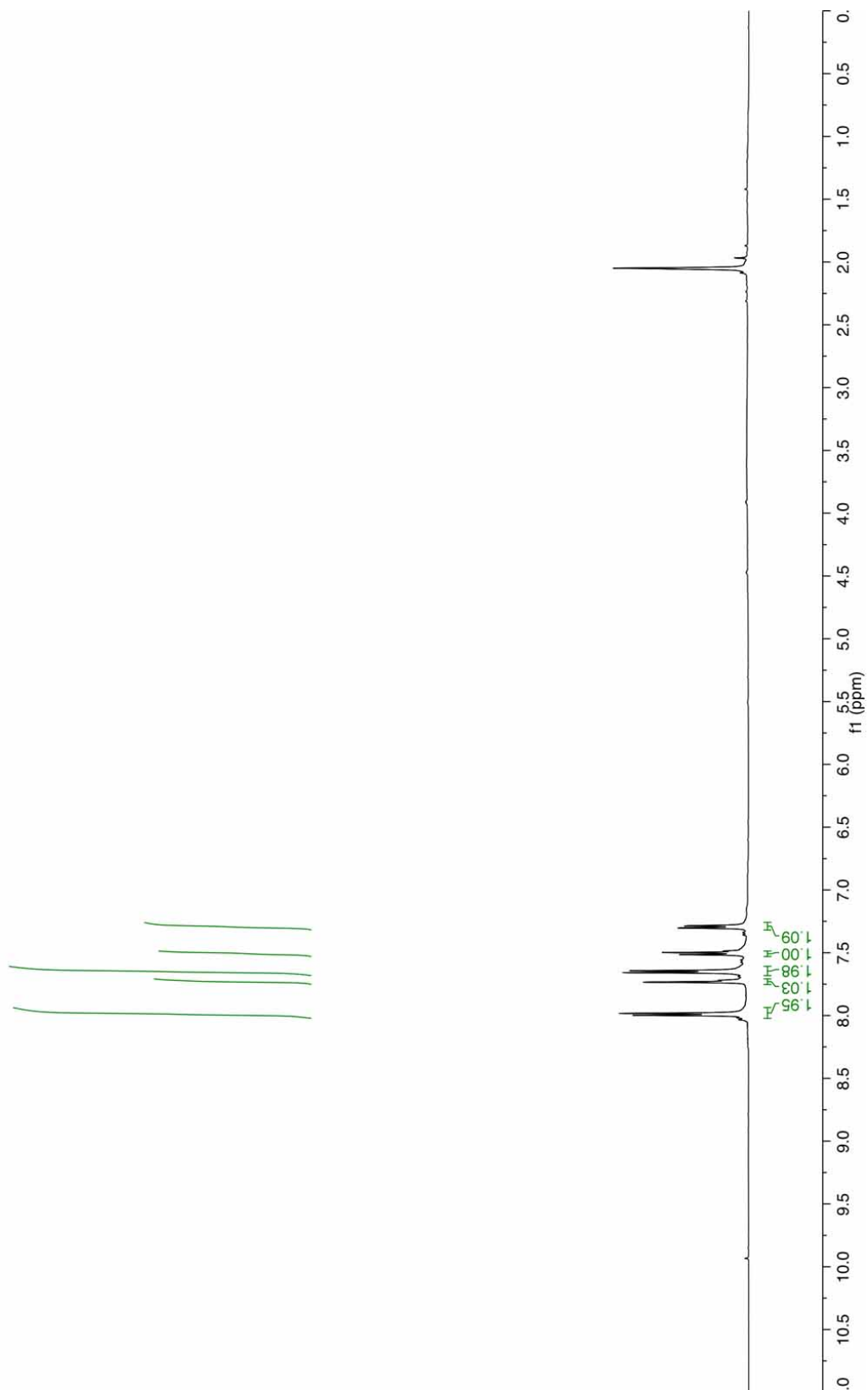
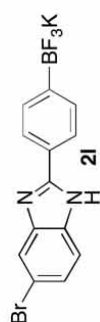
S66



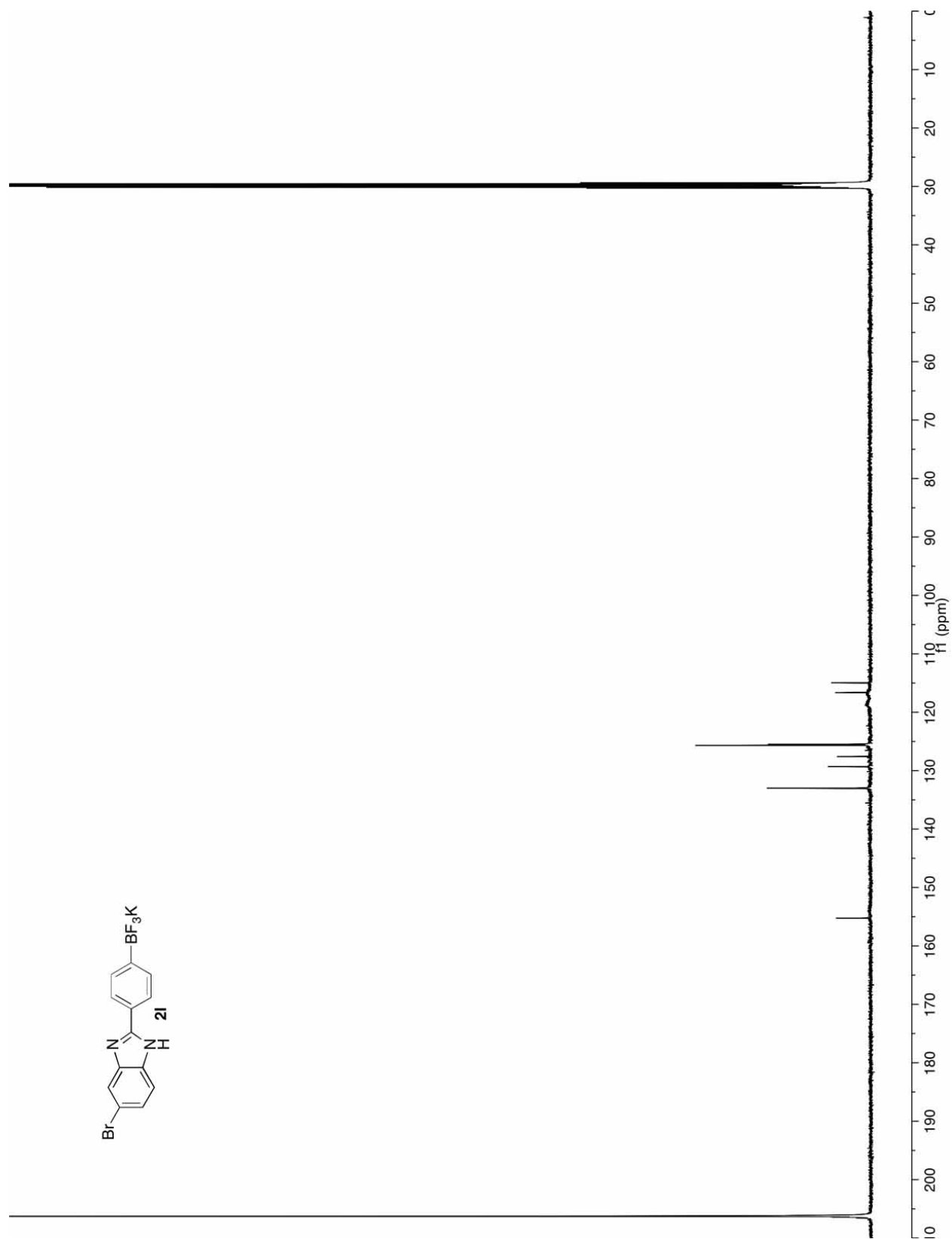
$^{19}\text{F}$  spectrum (470 MHz, acetone- $d_6$ ) of potassium (4-(5-Chloro-1*H*-benzo[*d*]imidazol-2-yl)phenyl)trifluoroborate (**2k**).



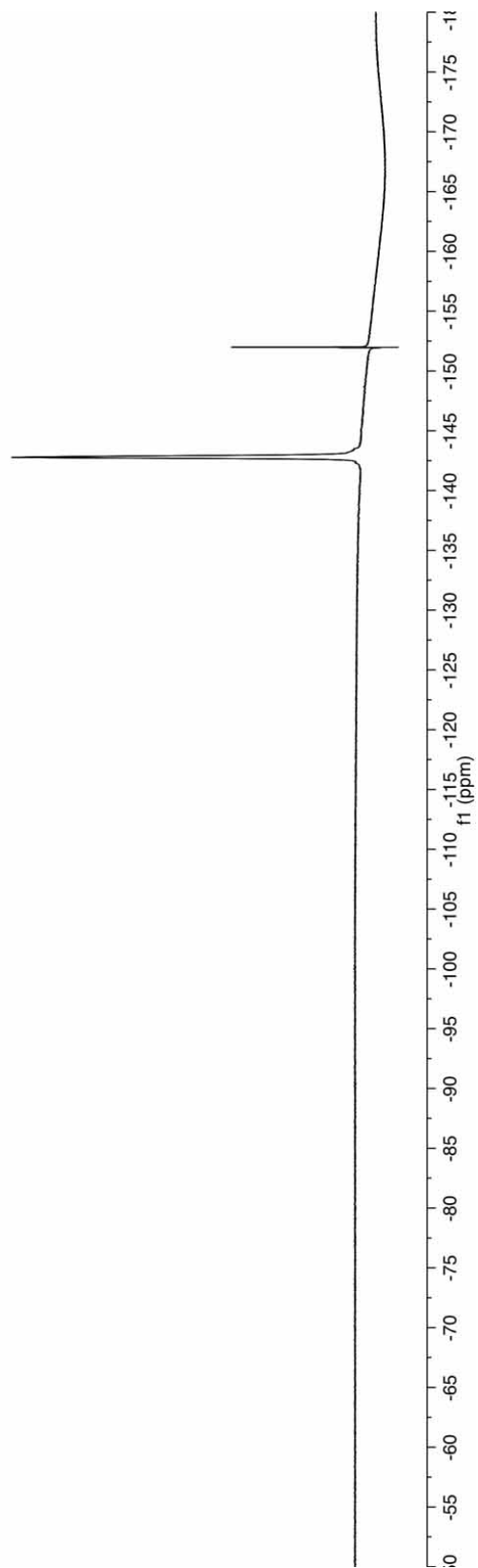
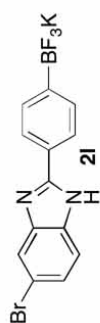
$^{11}\text{B}$  spectrum (128 MHz, acetone- $d_6$ ) of potassium 4-(5-Chloro-1H-benzo[d]imidazol-2-yl)phenyltrifluoroborate (**2k**).



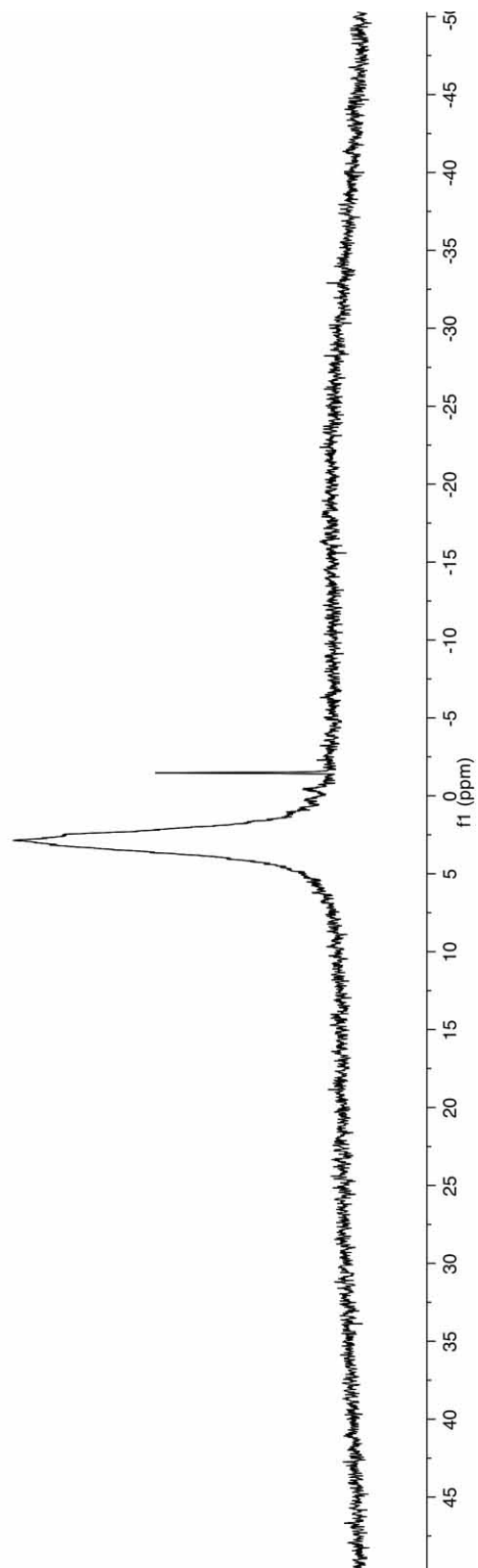
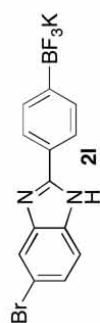
<sup>1</sup>H spectrum (500 MHz, acetone-*d*<sub>6</sub>) of potassium (4-(5-bromo-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**21**).



$^{13}\text{C}$  spectrum (125 MHz, acetone- $d_6$ ) of potassium (4-(5-Bromo-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**21**).

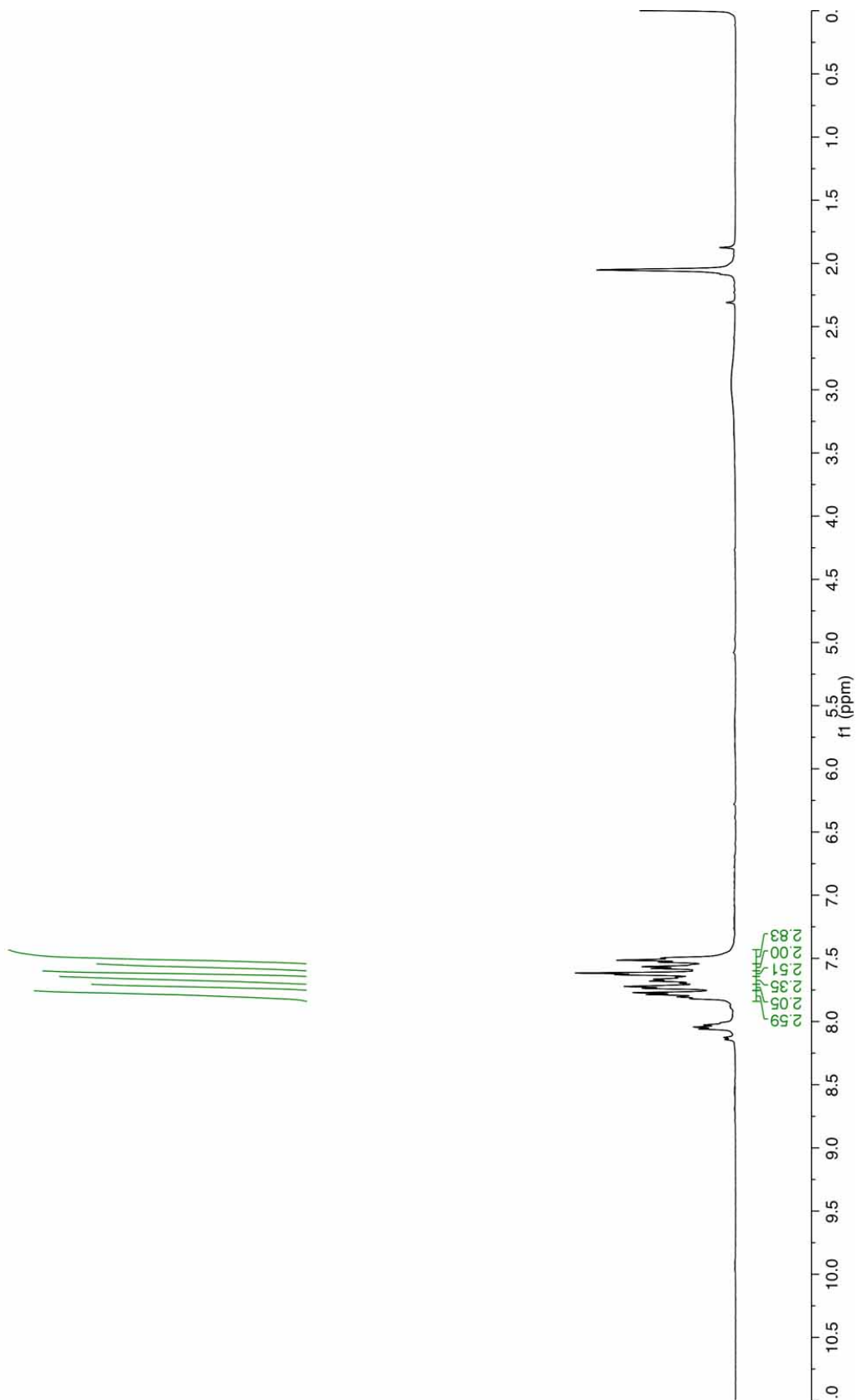
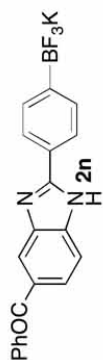


$^{19}\text{F}$  spectrum (470 MHz, acetone- $d_6$ ) of potassium (4-(5-Bromo-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**21**).

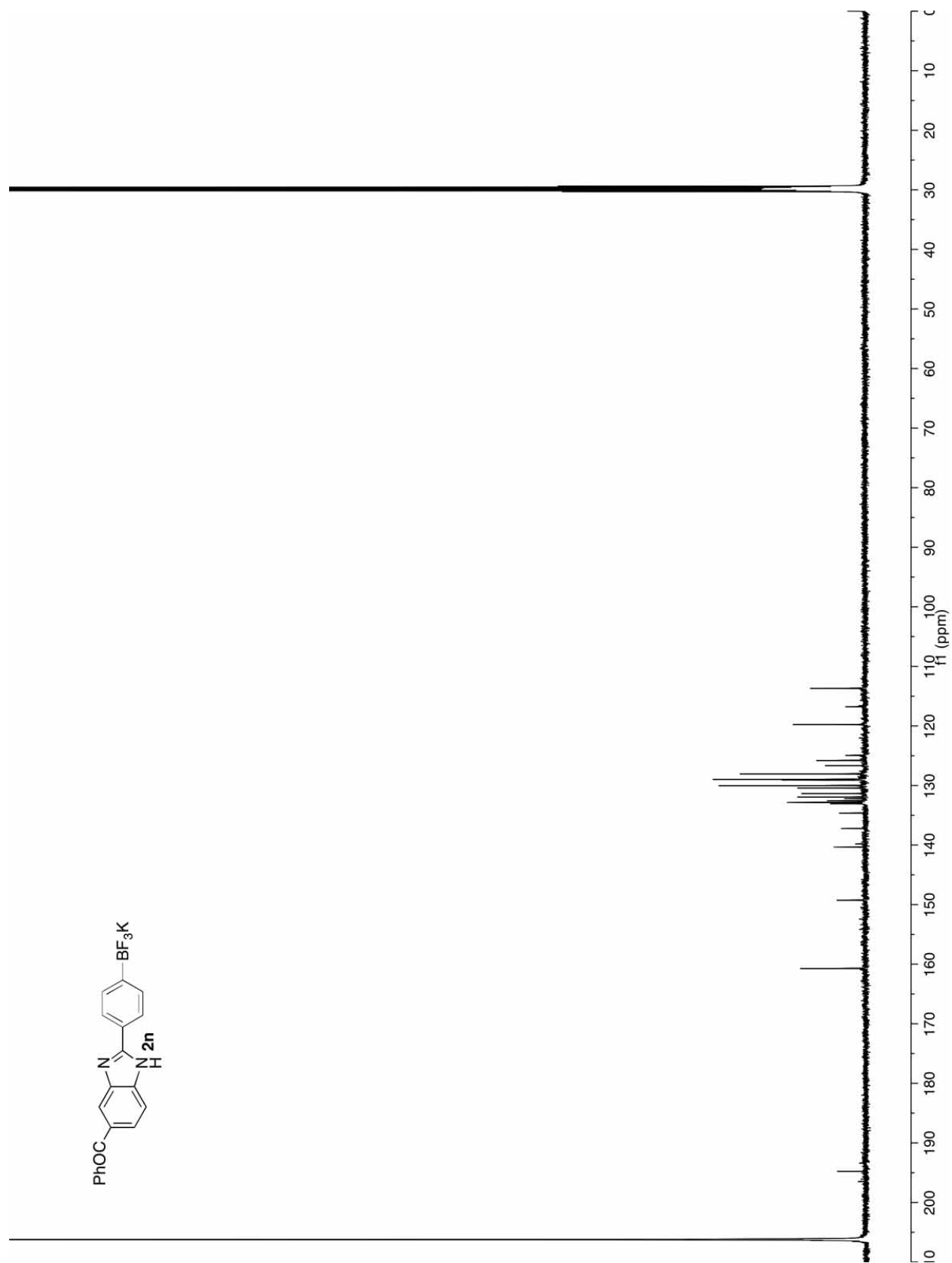


$^{11}\text{B}$  spectrum (128 MHz, acetone- $d_6$ ) of potassium (4-(5-bromo-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**21**).

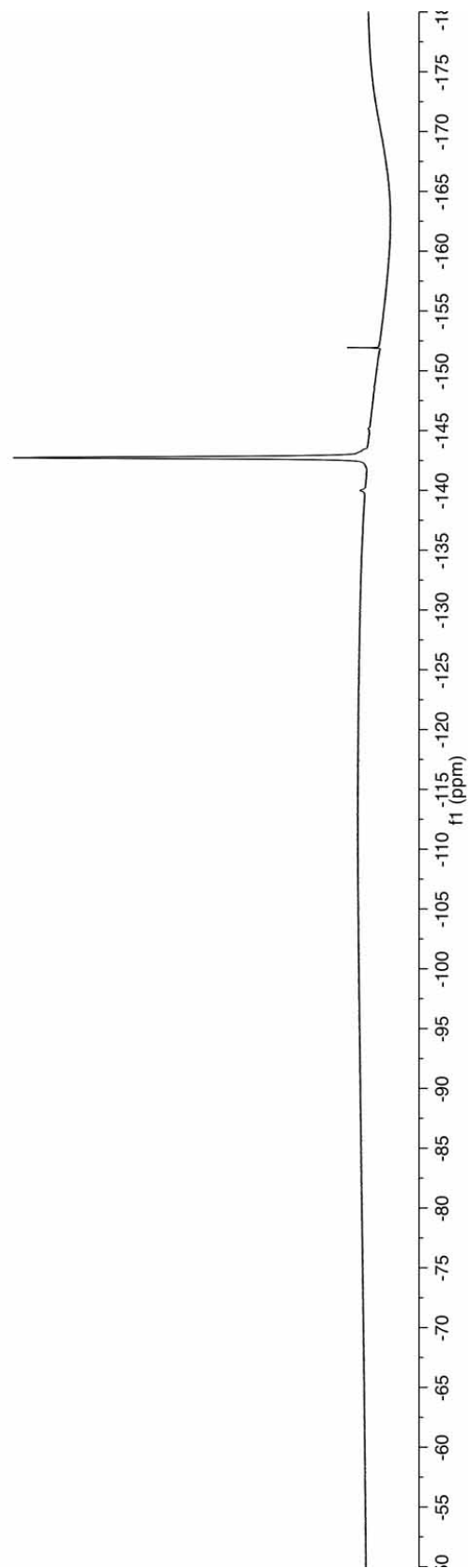
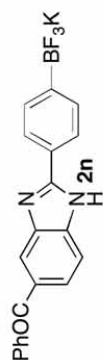




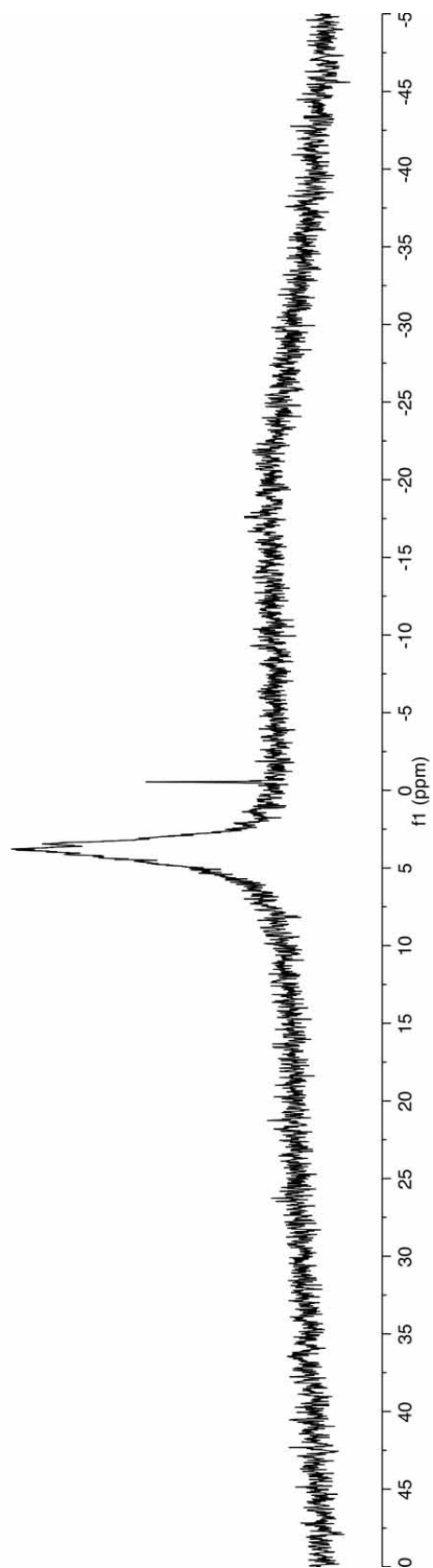
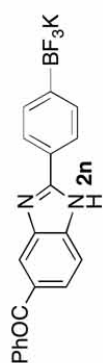
<sup>1</sup>H spectrum (500 MHz, acetone-*d*<sub>6</sub>) of potassium (4-(5-benzoyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl)trifluoroborate (**2n**).



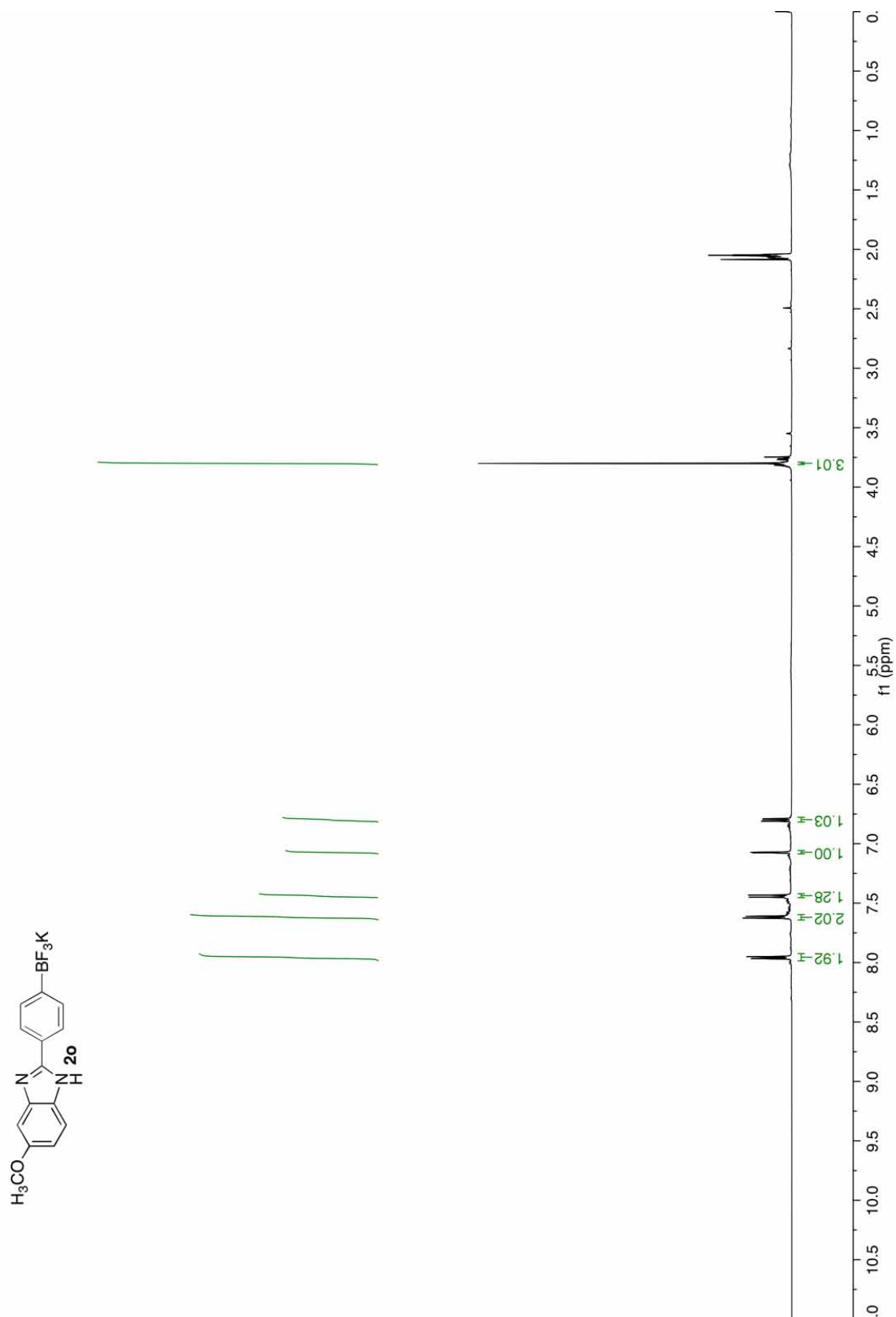
<sup>13</sup>C spectrum (125 MHz, acetone-*d*<sub>6</sub>) of potassium (4-(5-benzoyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl)trifluoroborate (**2n**).



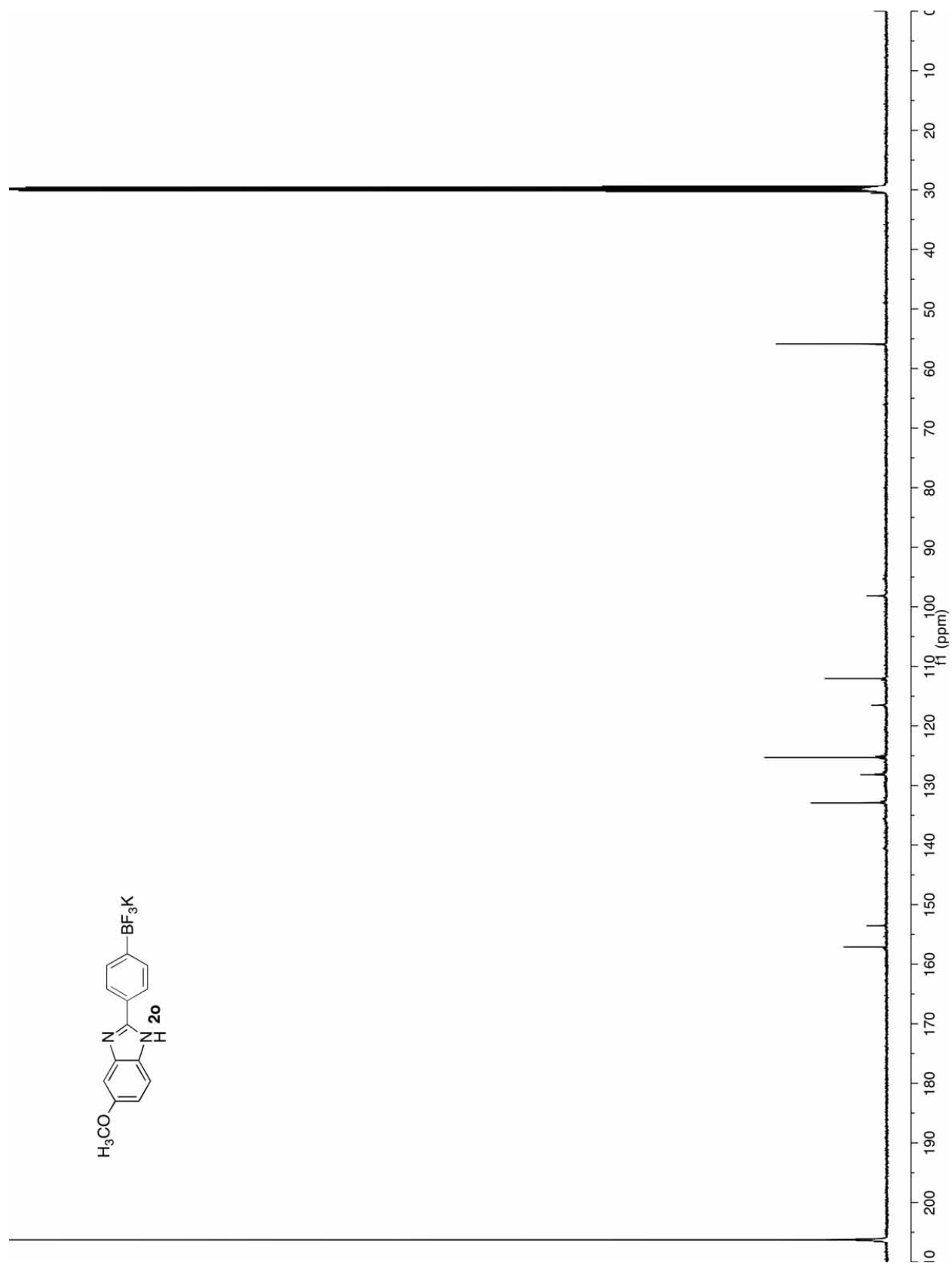
$^{19}\text{F}$  spectrum (470 MHz, acetone- $d_6$ ) of potassium (4-(5-benzoyl-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**2n**).



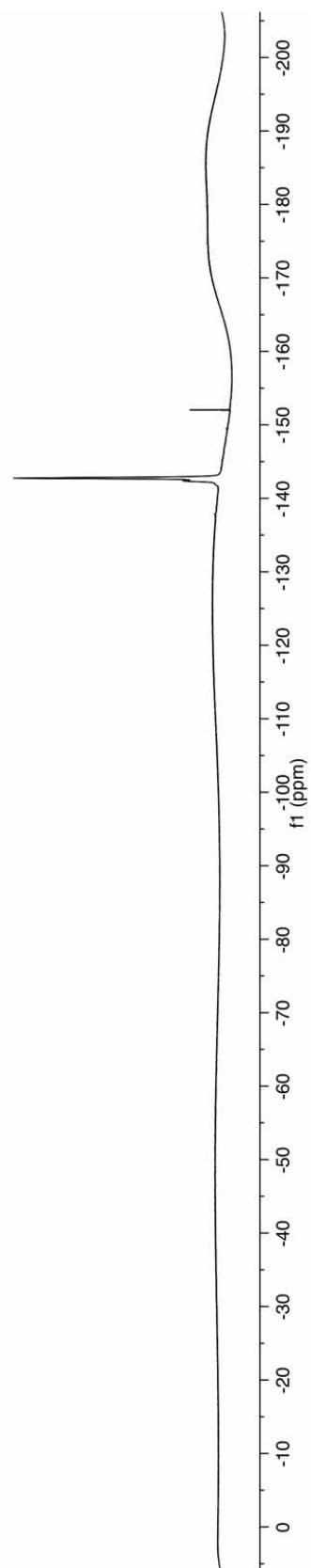
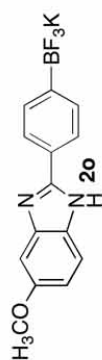
$^{11}\text{B}$  spectrum (128 MHz, acetone- $d_6$ ) of potassium (4-(5-benzoyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl)trifluoroborate (**2n**).



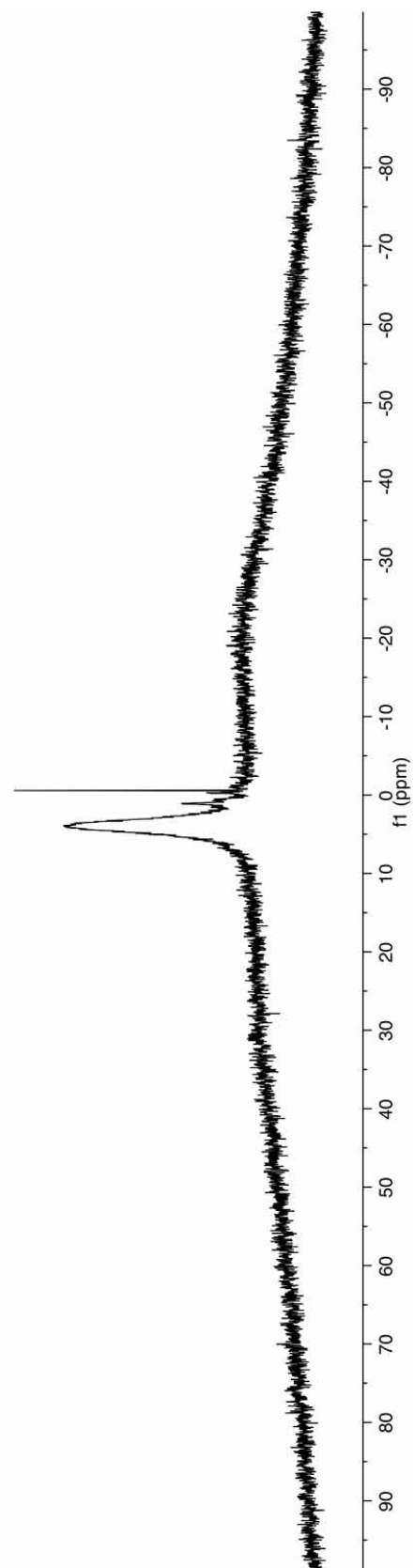
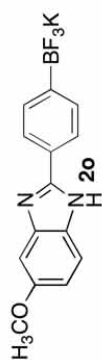
<sup>1</sup>H spectrum (500 MHz, acetone-*d*<sub>6</sub>) of potassium (4-(5-methoxy-1*H*-benzo[*d*]imidazol-2-yl)phenyl)trifluoroborate (**20**).



$^{13}\text{C}$  spectrum (125 MHz,  $\text{acetone-}d_6$ ) of potassium (4-(5-methoxy-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**20**).

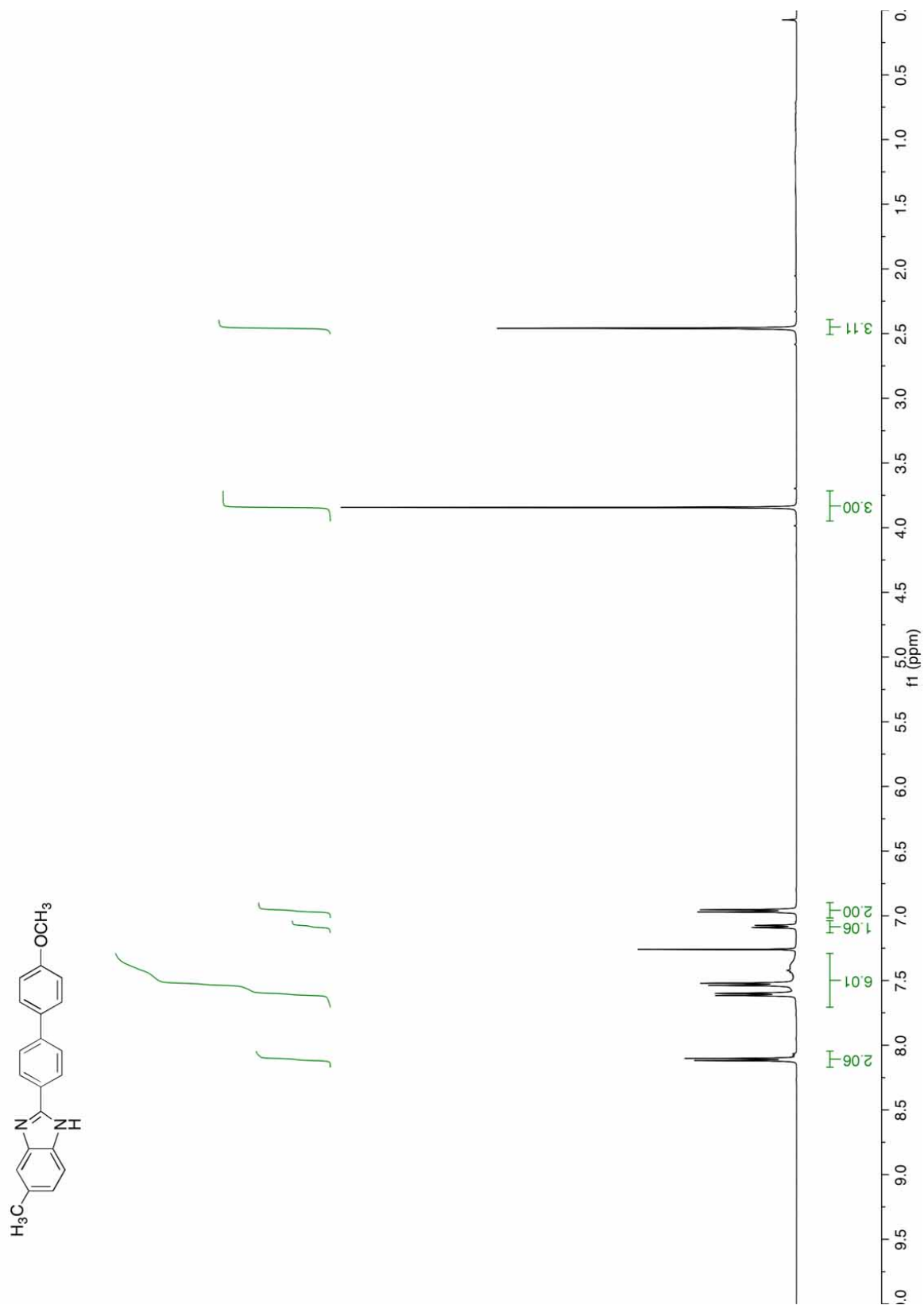


$^{19}\text{F}$  spectrum (470 MHz, acetone- $d_6$ ) of potassium (4-(5-methoxy-1H-benzo[d]imidazol-2-yl)phenyl)trifluoroborate (**20**).

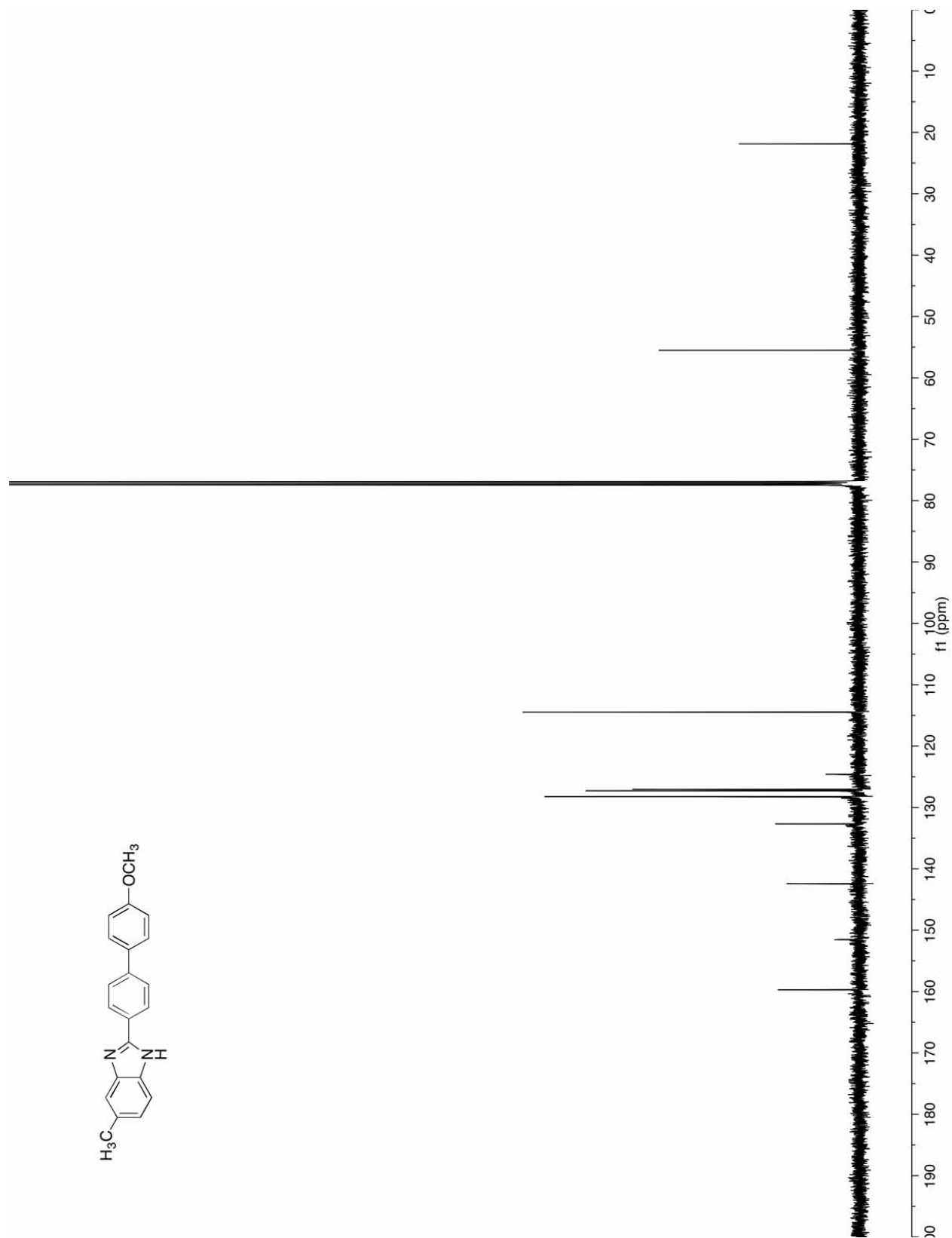


$^{11}\text{B}$  spectrum (128 MHz, acetone- $d_6$ ) of potassium (4-(5-methoxy-1*H*-benzo[*d*]imidazol-2-yl)phenyl)trifluoroborate (**20**).

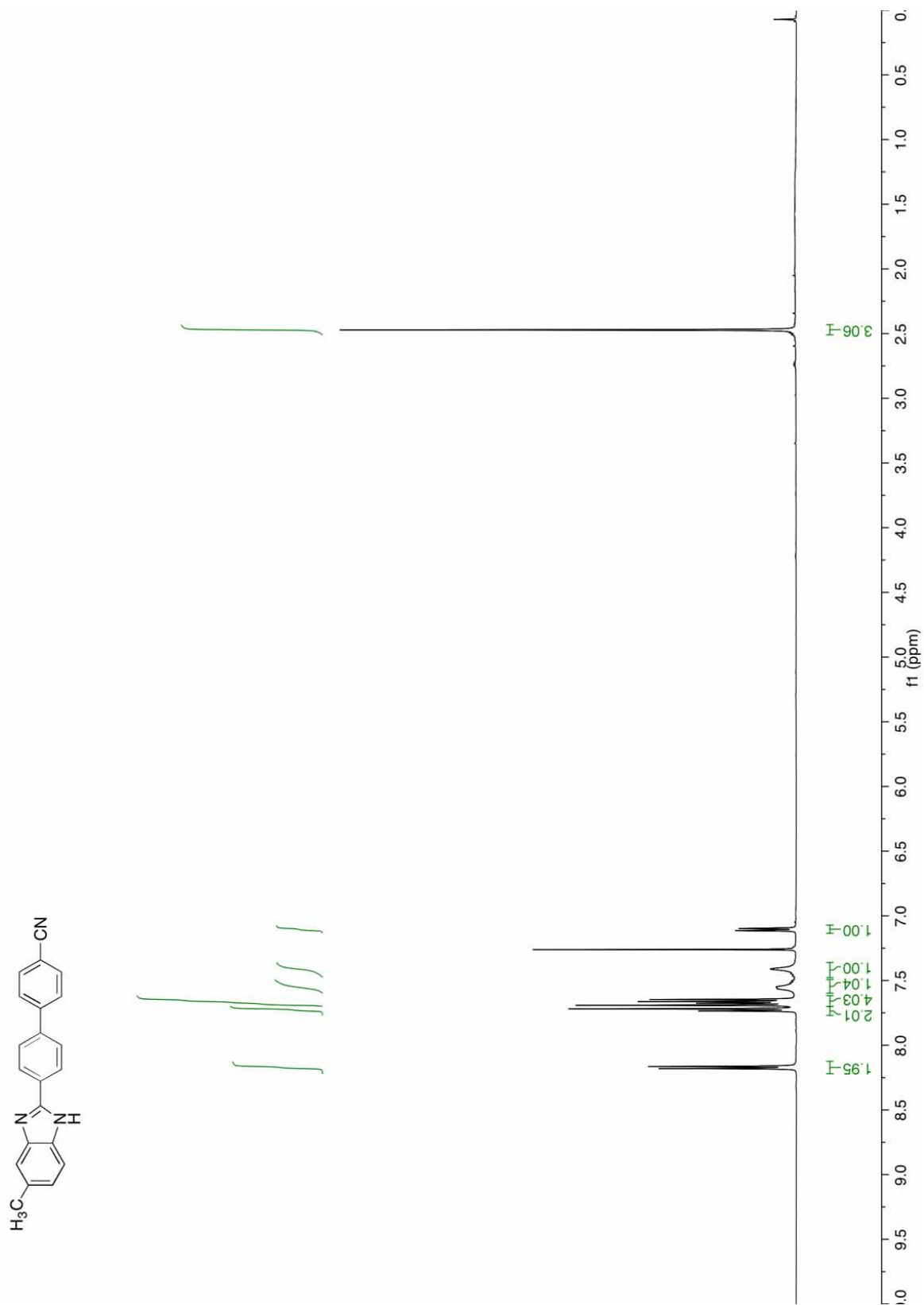




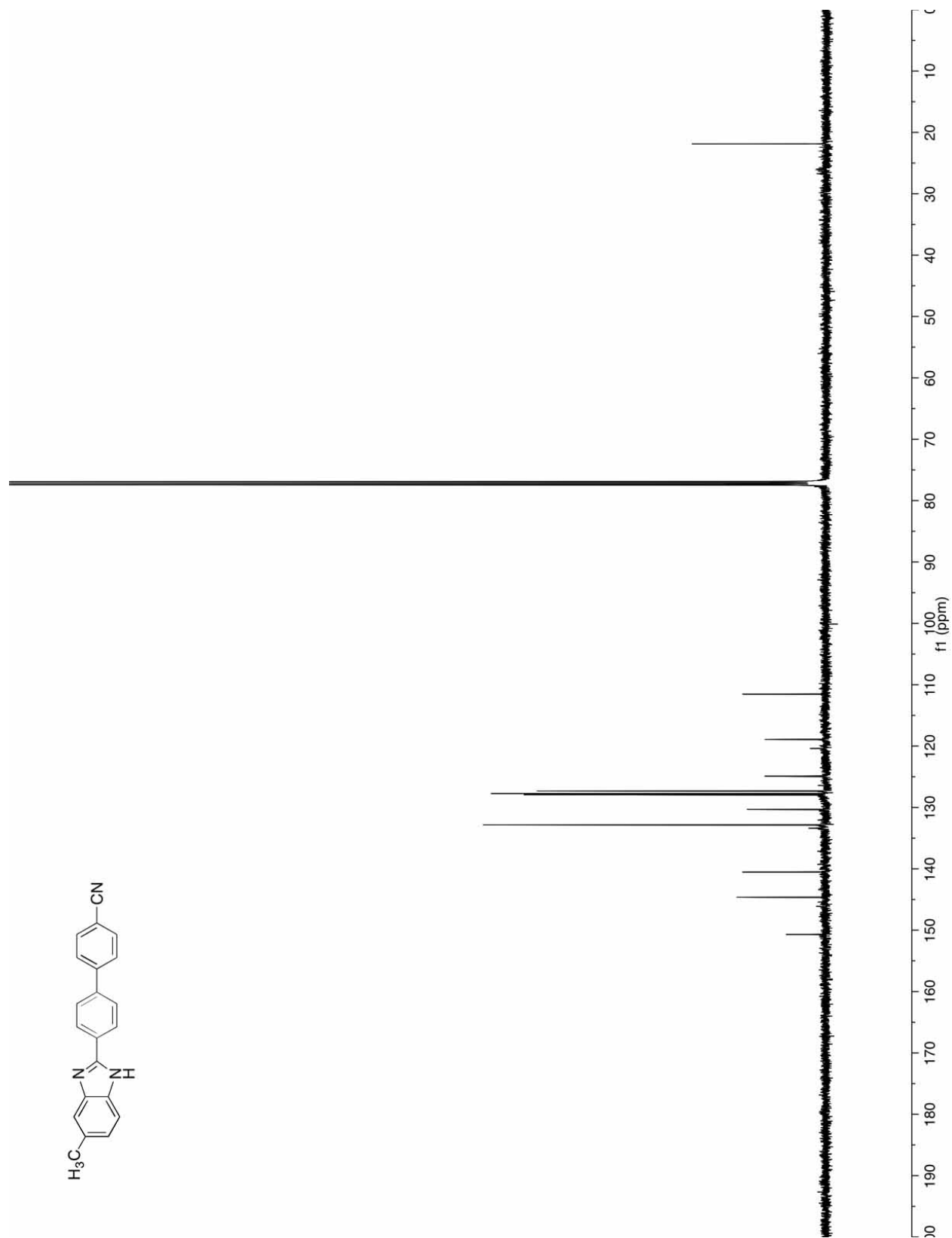
<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of 2-(4'-Methoxy-[1,1'-biphenyl]-4-yl)-5-methyl-1H-benzo[d]imidazole.



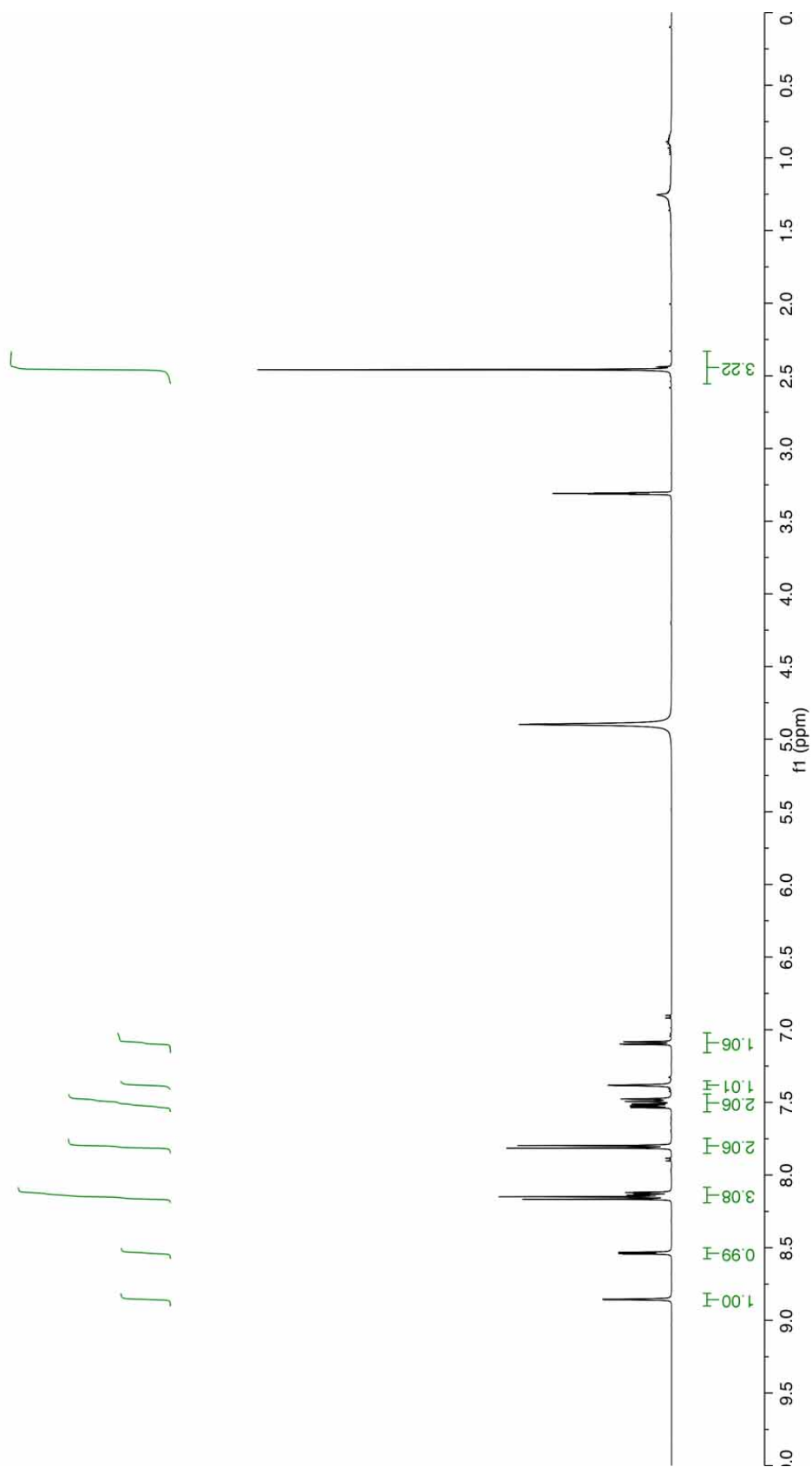
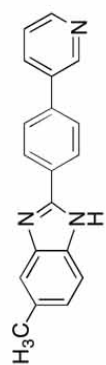
<sup>13</sup>C spectrum (125 MHz, CDCl<sub>3</sub>) of 2-(4'-Methoxy-[1,1'-biphenyl]-4-yl)-5-methyl-1H-benzo[d]imidazole.



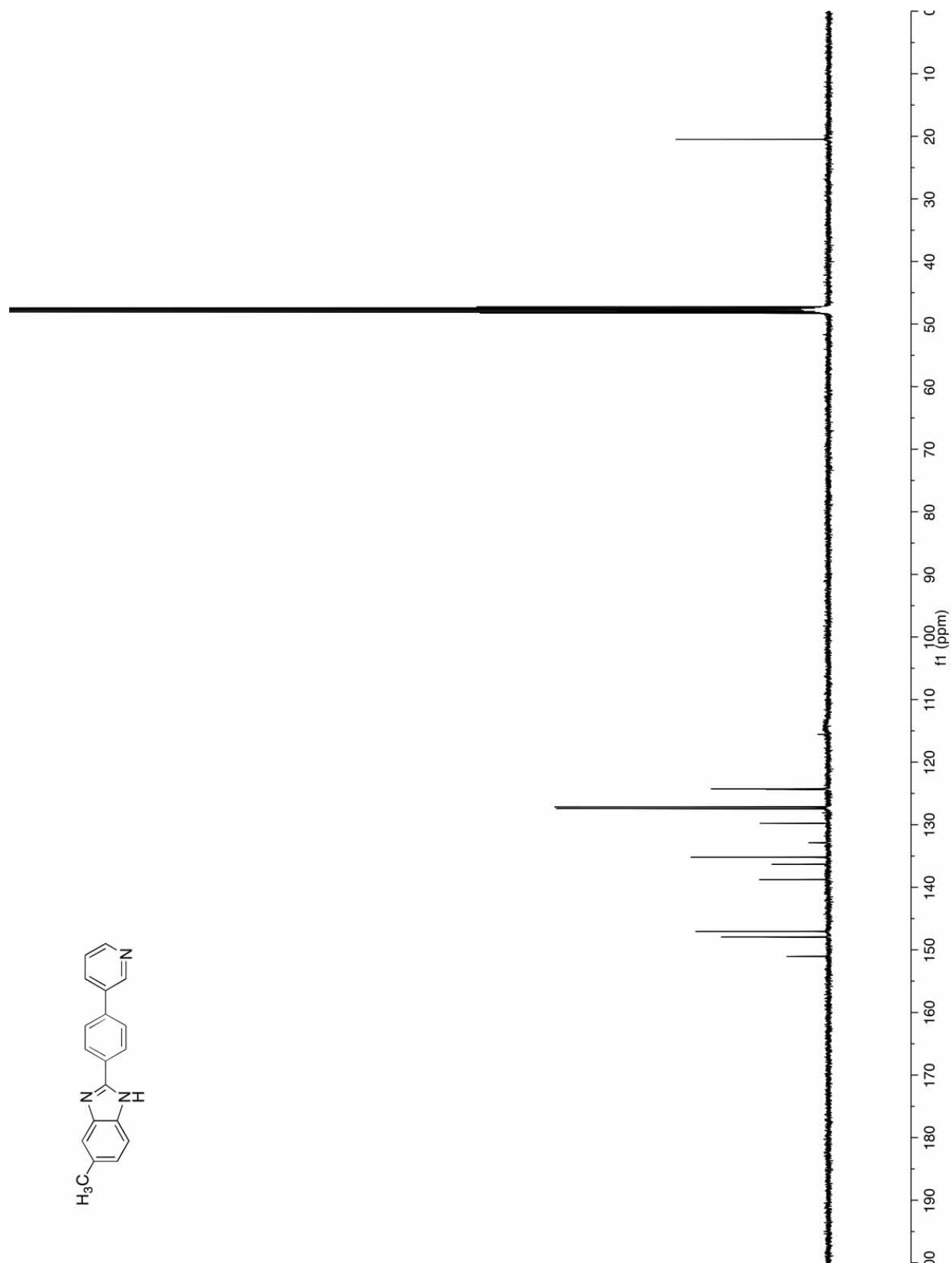
<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of 4'-(5-Methyl-1H-benzo[d]imidazol-2-yl)-[1,1'-biphenyl]-4-carbonitrile.



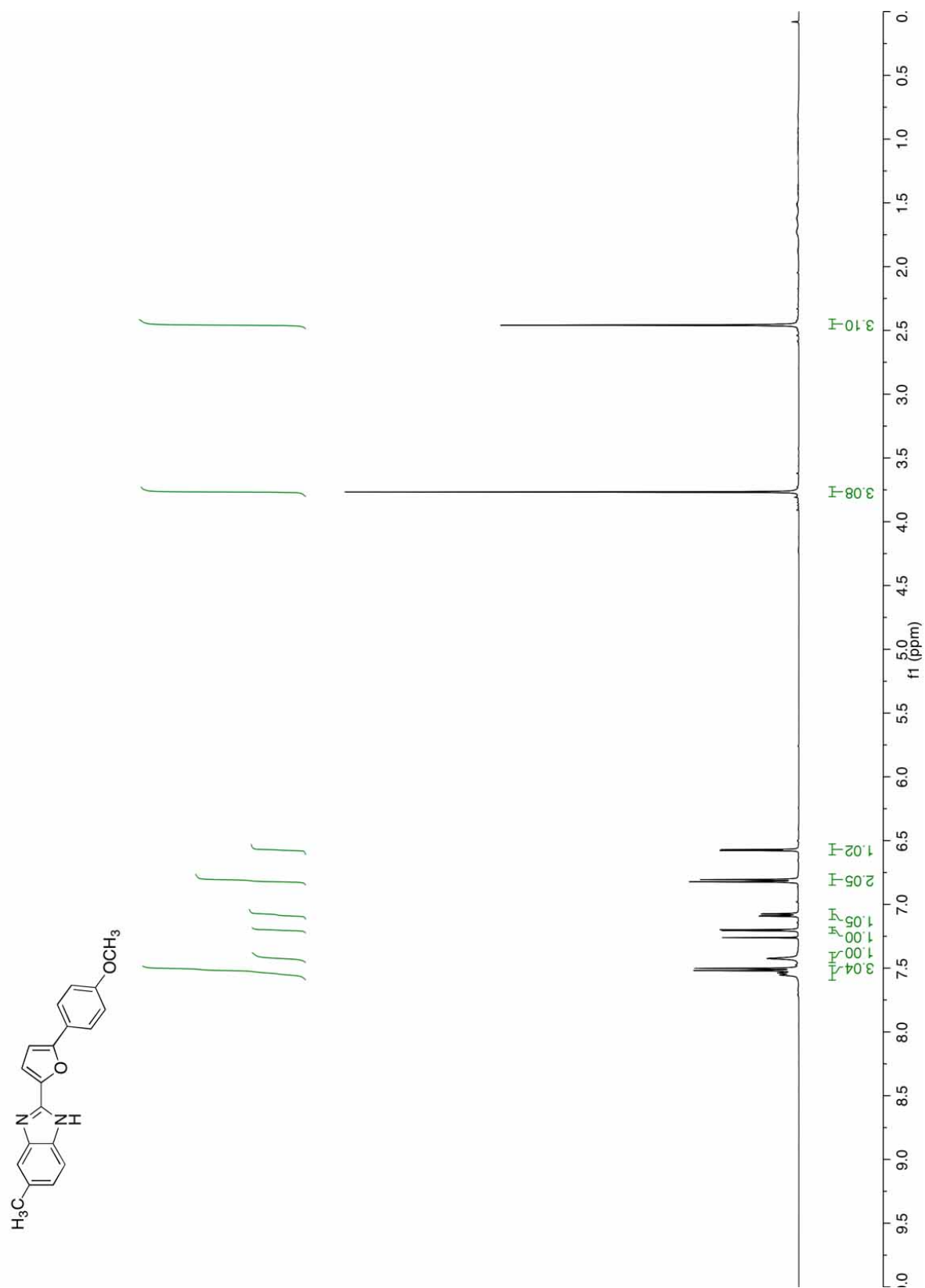
<sup>13</sup>C spectrum (125 MHz, CDCl<sub>3</sub>) of 4'-(5-Methyl-1H-benzo[d]imidazol-2-yl)-[1,1'-biphenyl]-4-carbonitrile.



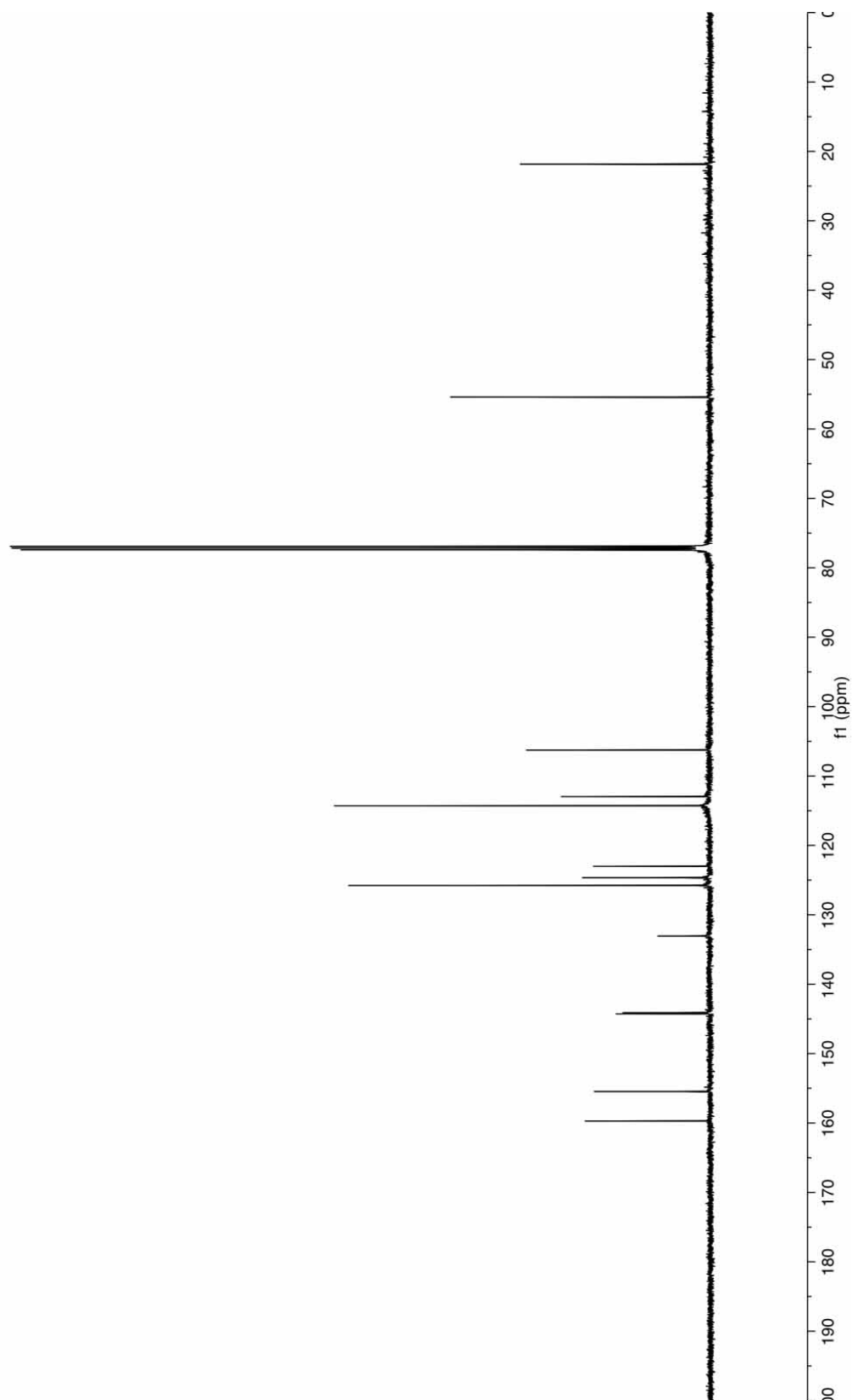
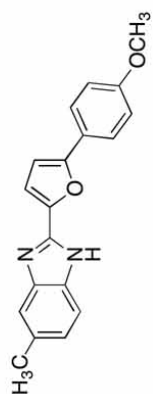
<sup>1</sup>H spectrum (500 MHz, CD<sub>3</sub>OD) of 5-Methyl-2-(4-(pyridin-3-yl)phenyl)-1H-benzo[d]imidazole.



<sup>13</sup>C spectrum (125 MHz, CD<sub>3</sub>OD) of 5-methyl-2-(4-(pyridin-3-yl)phenyl)-1*H*-benzo[*d*]imidazole.

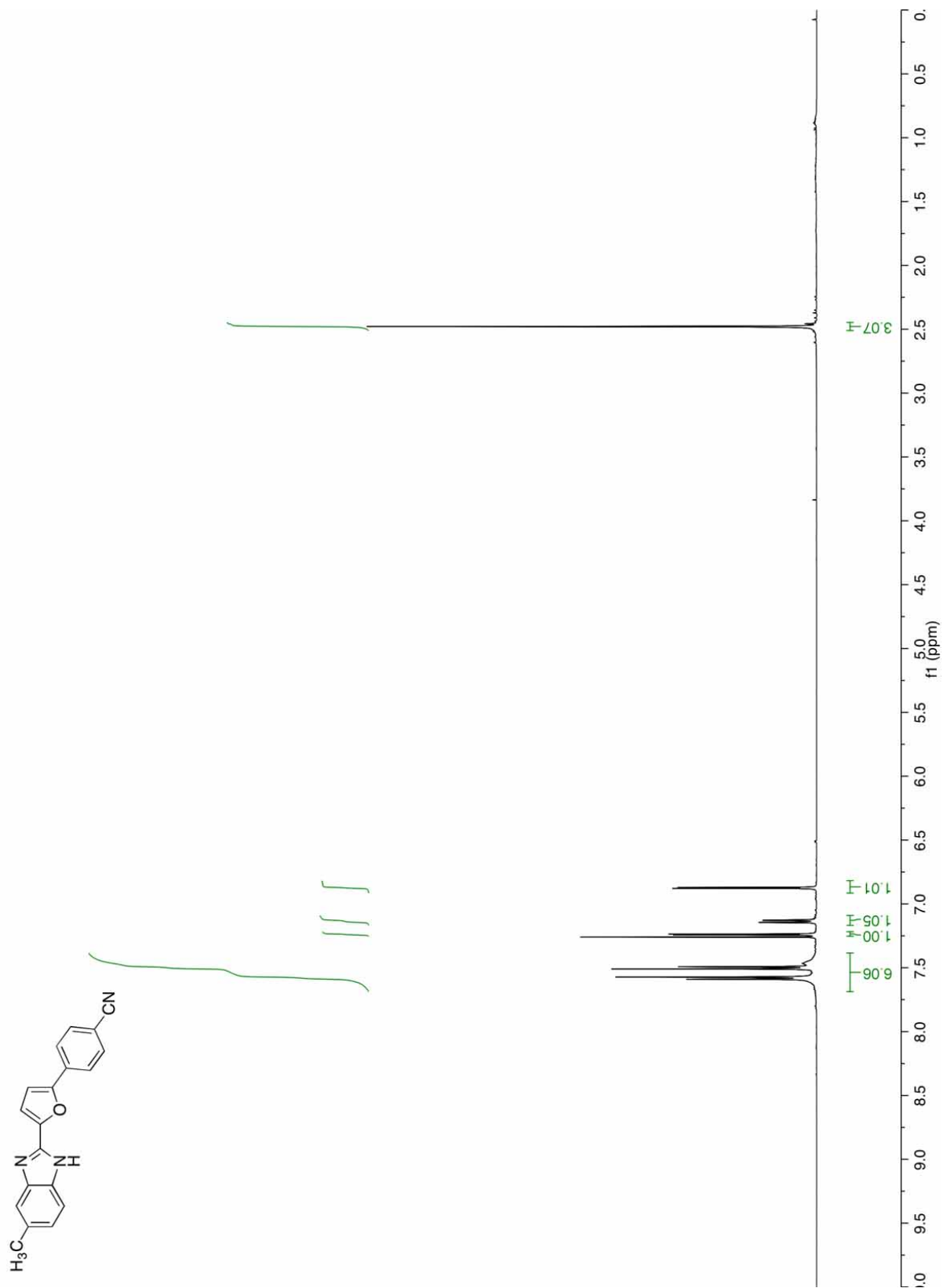


<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of 2-(5-(4-methoxyphenyl)furan-2-yl)-5-methyl-1H-benzo[d]imidazole.

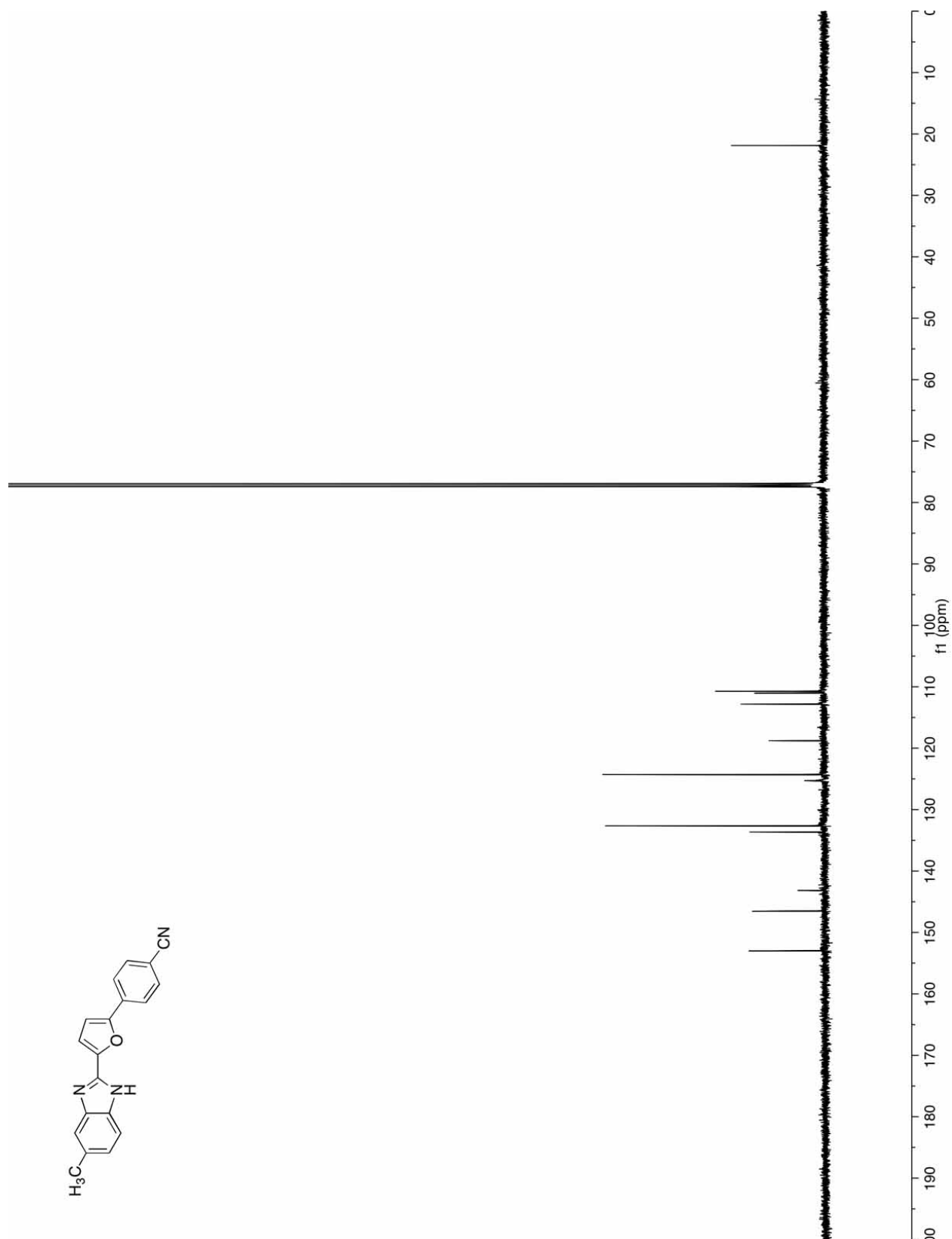


<sup>13</sup>C spectrum (125 MHz, CDCl<sub>3</sub>) of 2-(5-(4-Methoxyphenyl)furan-2-yl)-5-methyl-1H-benzo[d]imidazole.

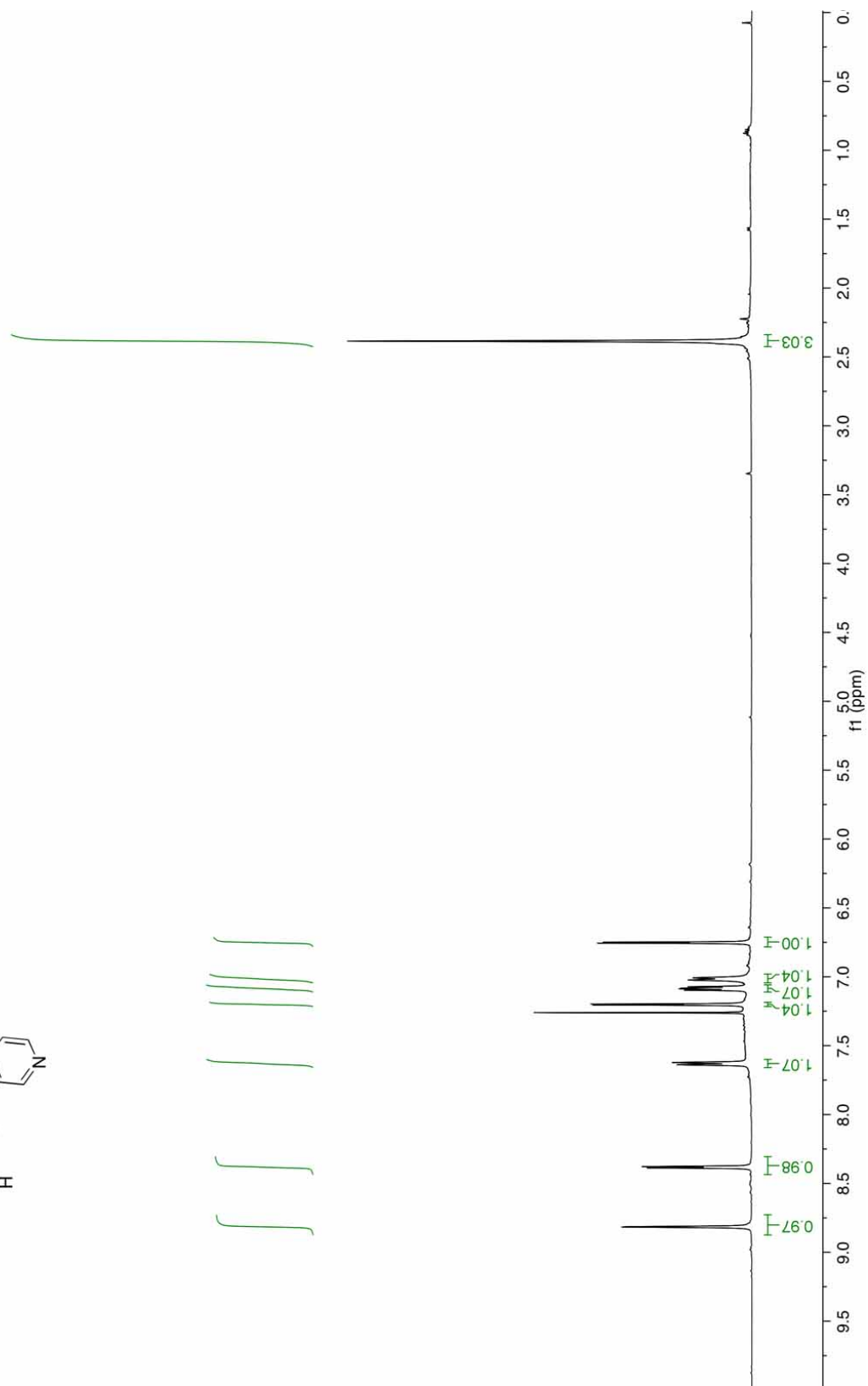
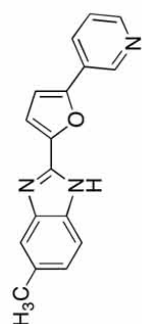




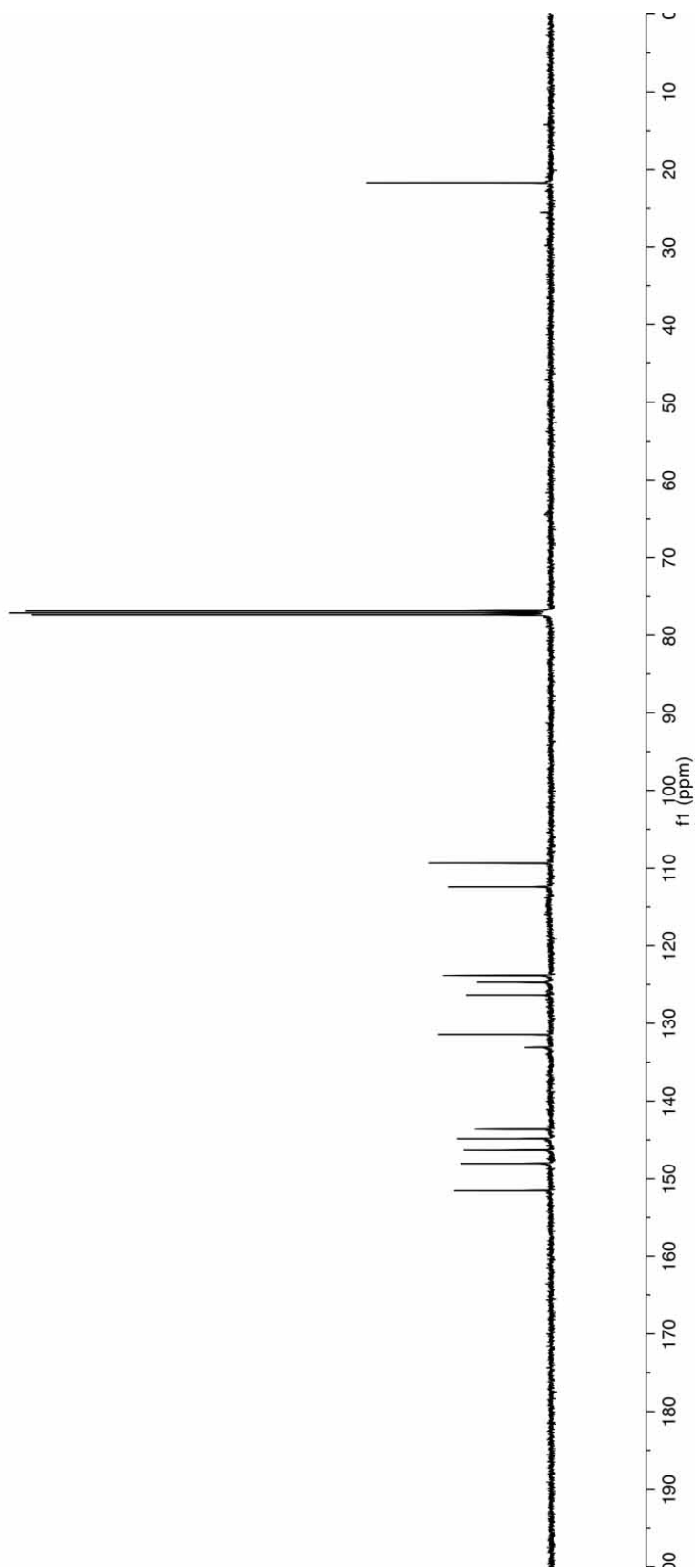
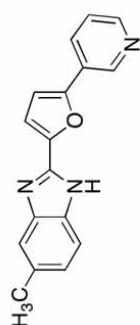
<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of 4-(5-(5-Methyl-1*H*-benzo[*d*]imidazol-2-yl)furan-2-yl)benzonitrile.



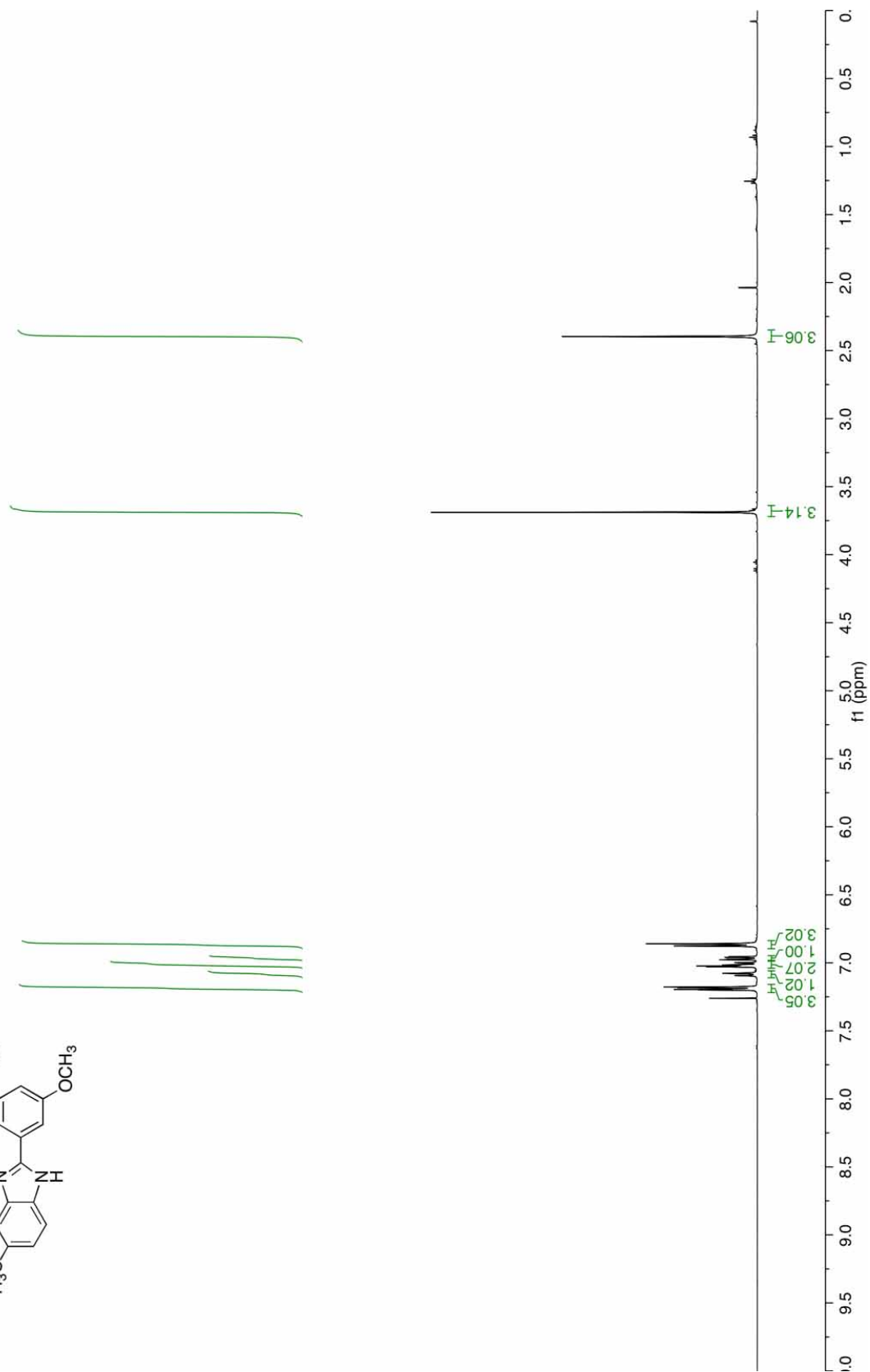
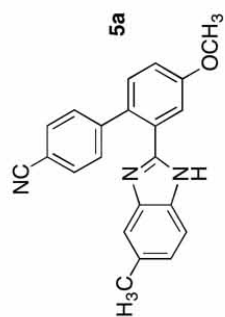
<sup>13</sup>C spectrum (125 MHz, CDCl<sub>3</sub>) of 4-(5-(5-Methyl-1H-benzo[d]imidazol-2-yl)furan-2-yl)benzonitrile.



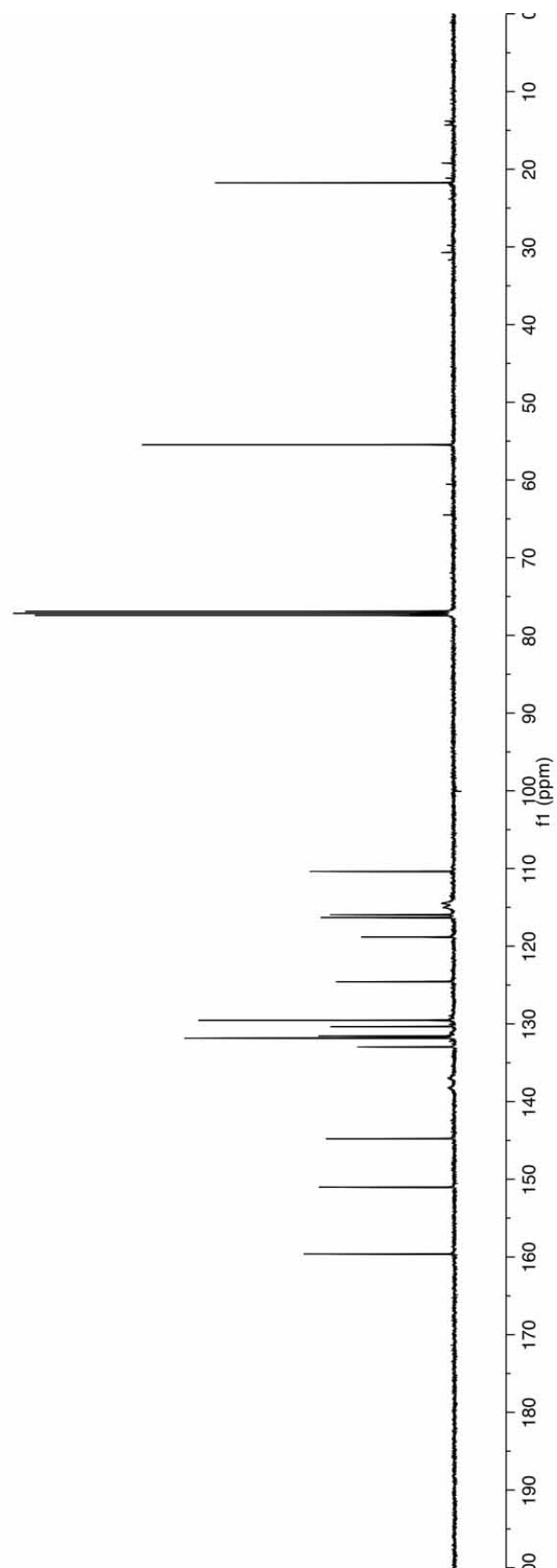
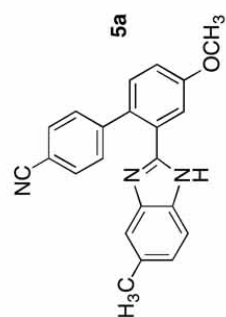
<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of 5-Methyl-2-(5-(pyridin-3-yl)furan-2-yl)-1H-benzo[d]imidazole.



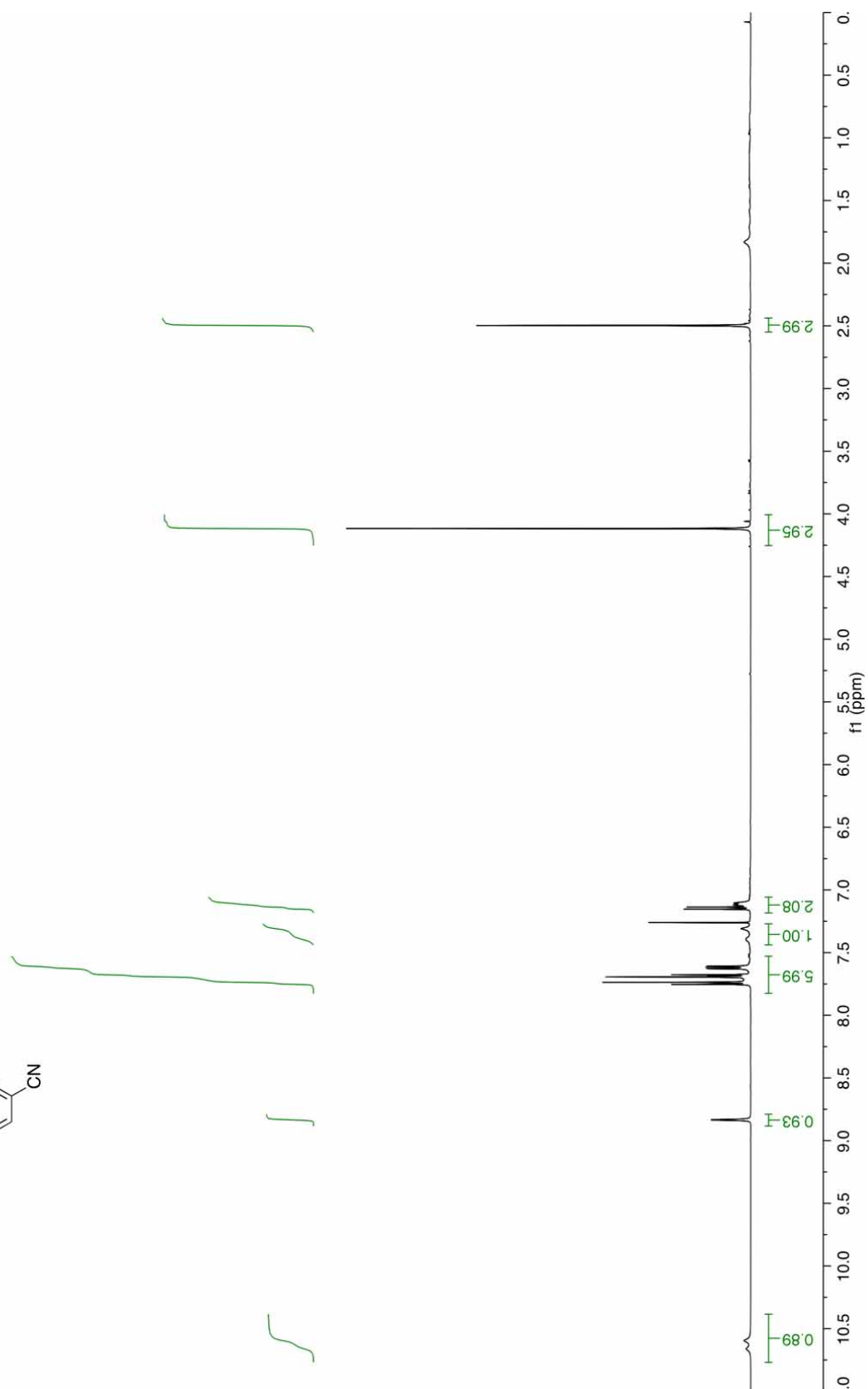
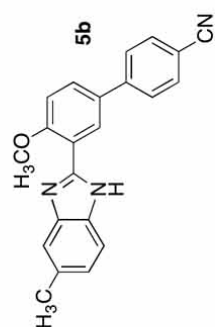
<sup>13</sup>C spectrum (125 MHz, CDCl<sub>3</sub>) of 5-Methyl-2-(5-(pyridin-3-yl)furan-2-yl)-1H-benzo[d]imidazole.



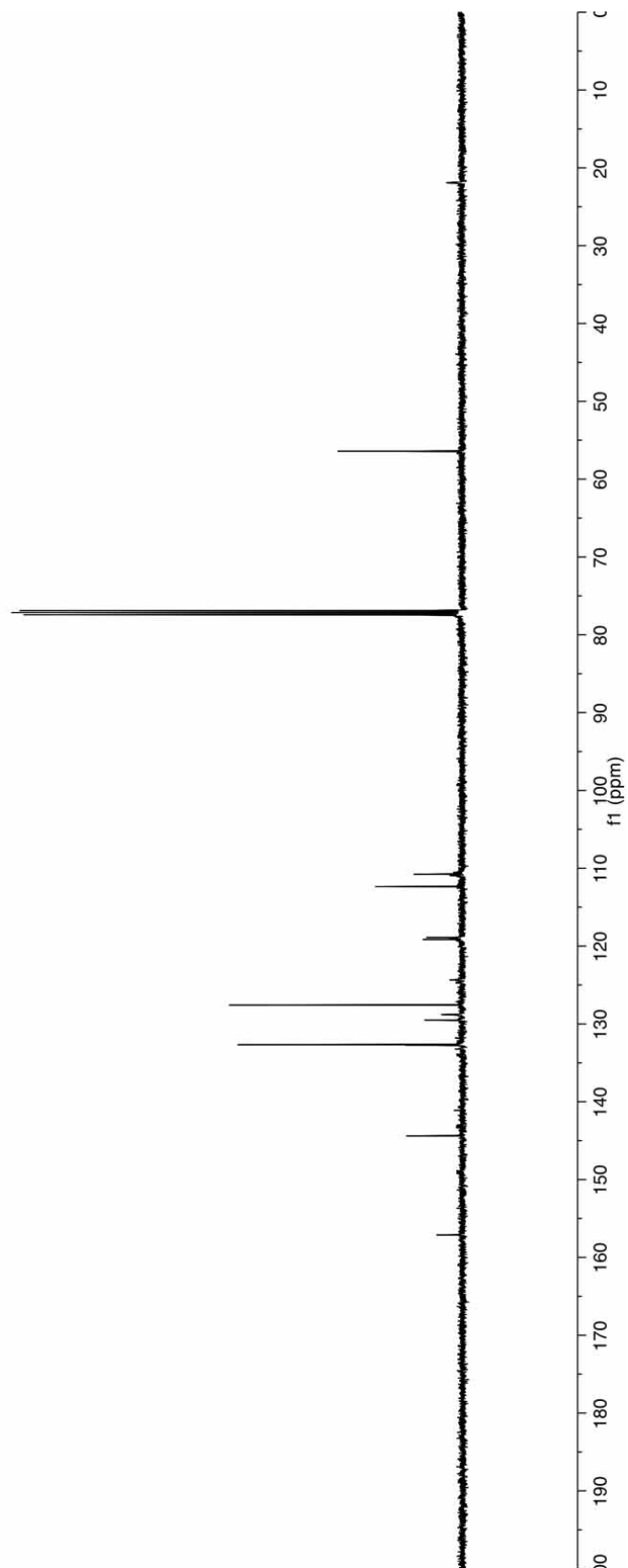
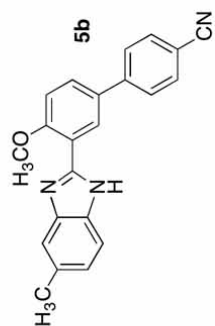
<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of 4'-Methoxy-2'-(5-methyl-1*H*-benzo[*d*]imidazol-2-yl)-[1,1'-biphenyl]-4-carbonitrile (**5a**).



<sup>13</sup>C spectrum (125 MHz, CDCl<sub>3</sub>) of 4'-Methoxy-2'-(5-methyl-1*H*-benzo[*d*]imidazol-2-yl)-[1,1'-biphenyl]-4-carbonitrile (**5a**).

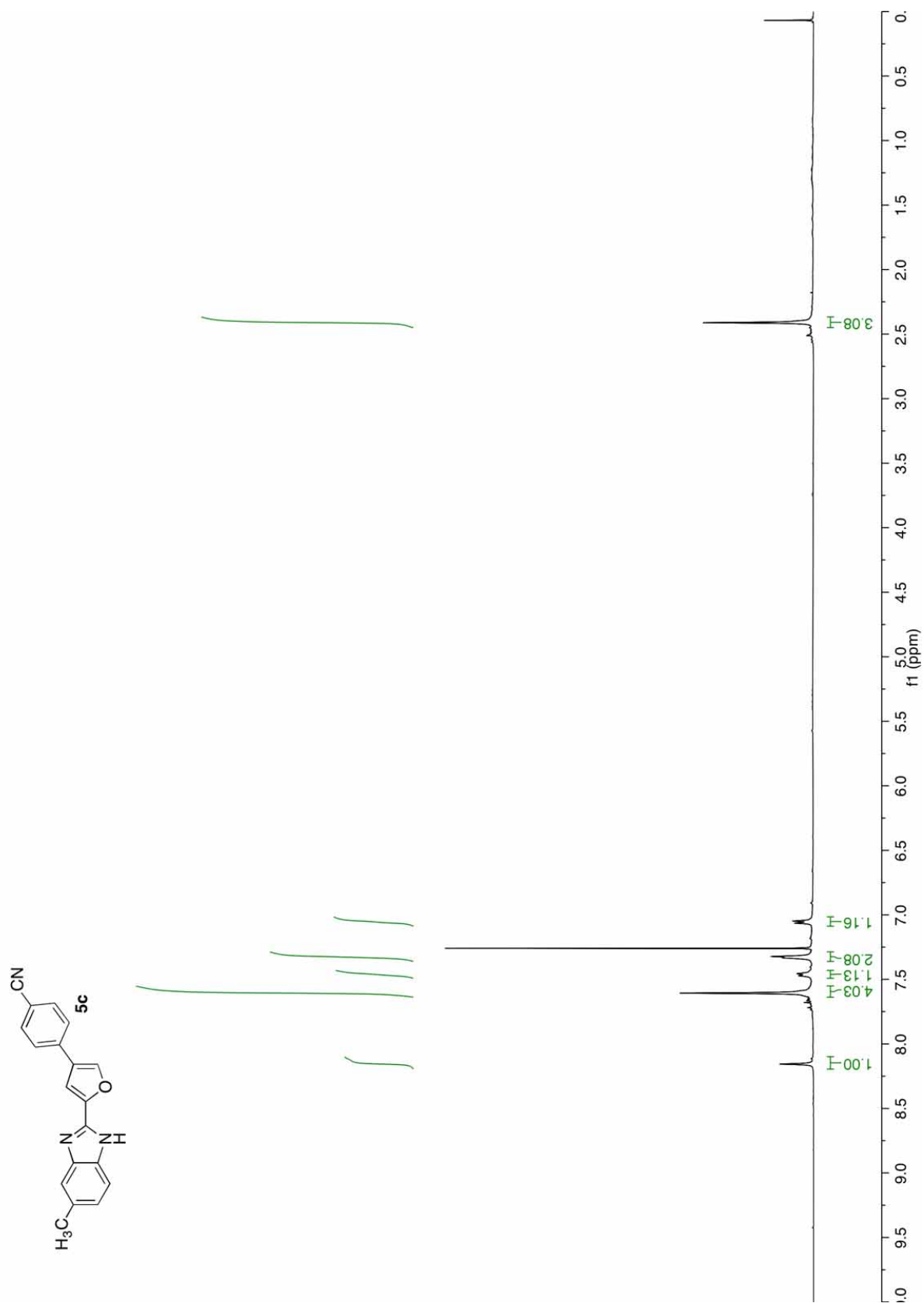


$^1\text{H}$  spectrum (500 MHz,  $\text{CDCl}_3$ ) of 4'-Methoxy-3'-(5-methyl-1*H*-benzo[*d*]imidazol-2-yl)-[1,1'-biphenyl]-4-carbonitrile (**5b**).

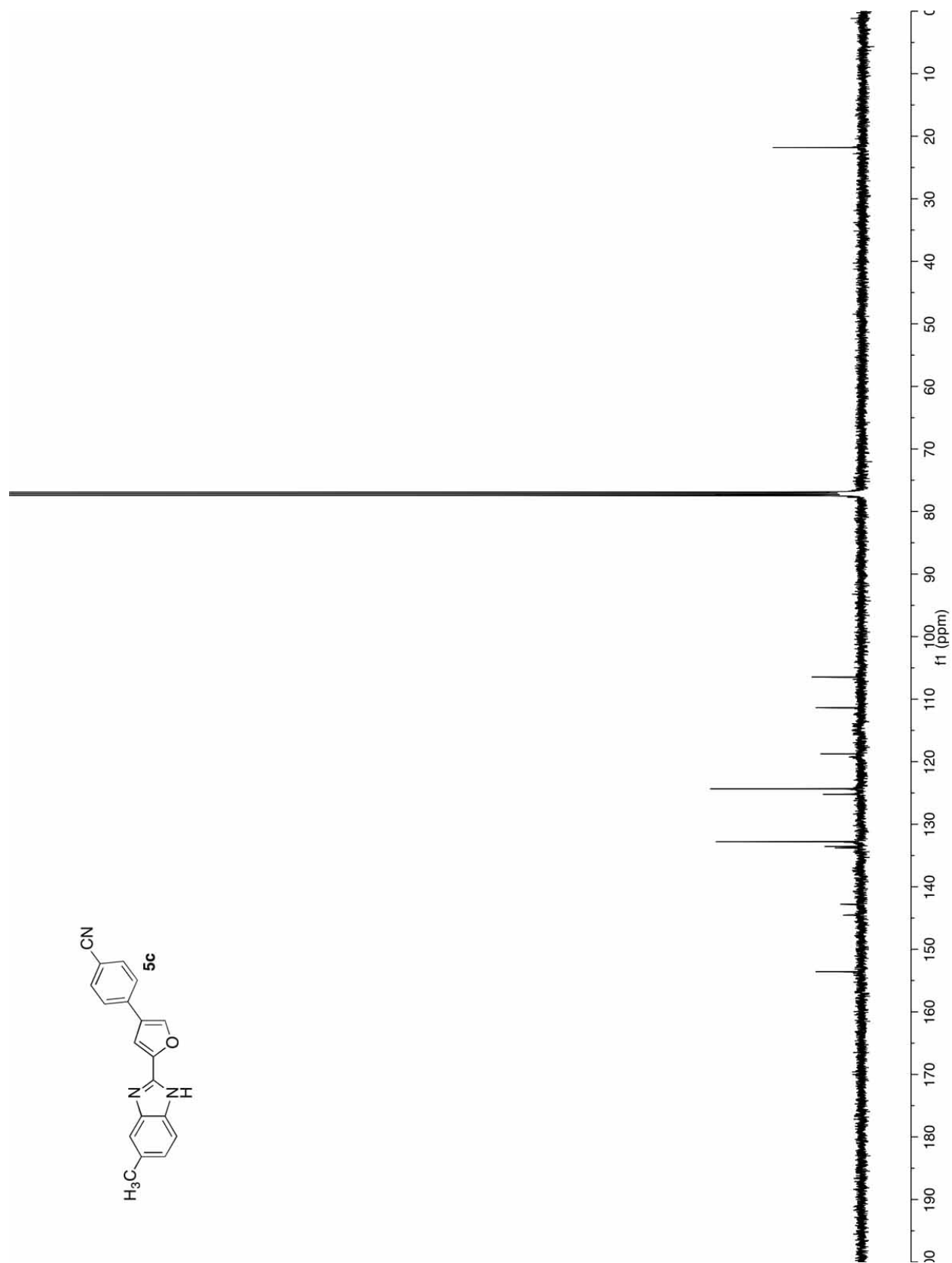


<sup>13</sup>C spectrum (125 MHz, CDCl<sub>3</sub>) of 4'-Methoxy-3'-(5-methyl-1H-benzo[d]imidazol-2-yl)-[1,1'-biphenyl]-4-carbonitrile (**5b**).

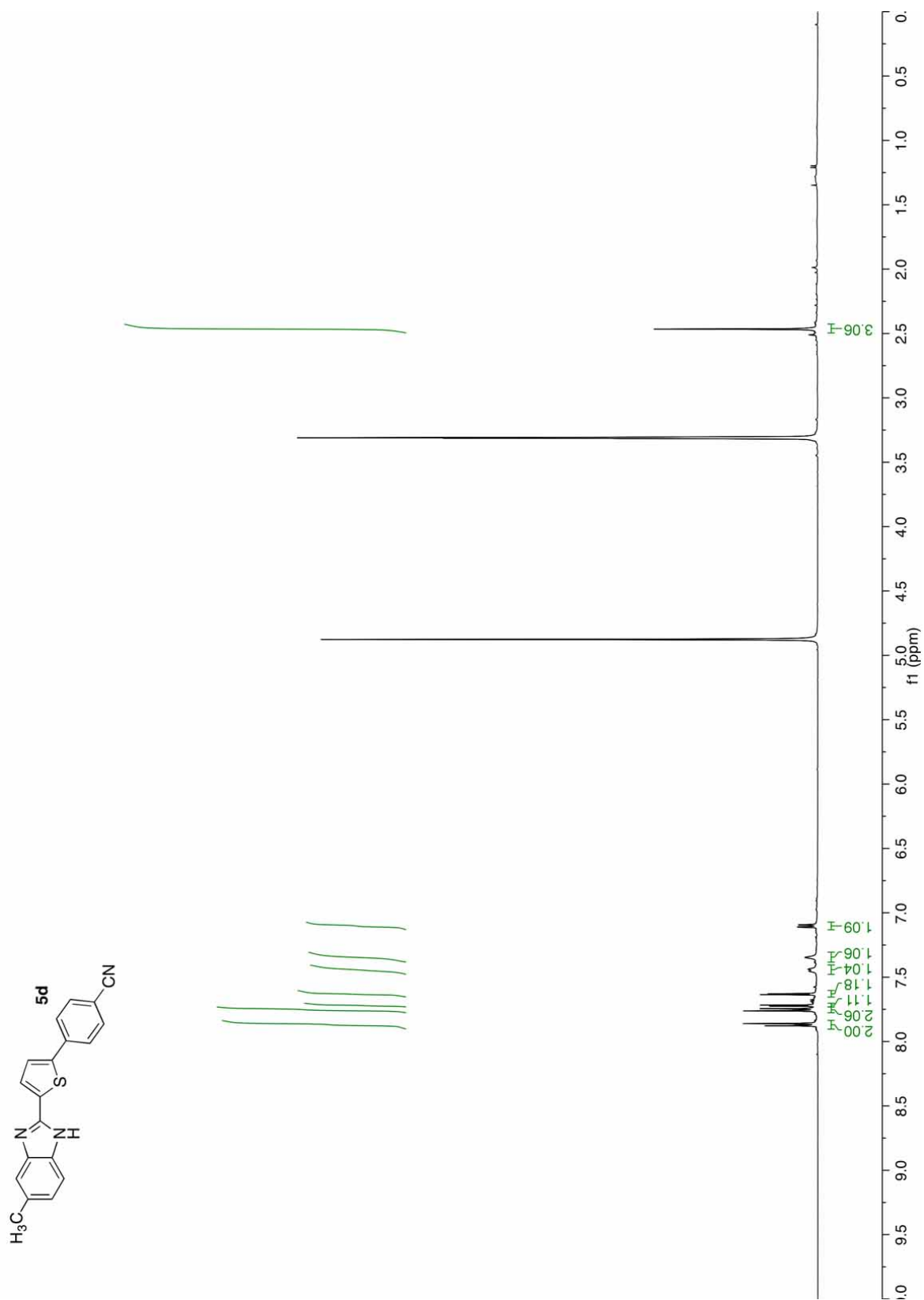




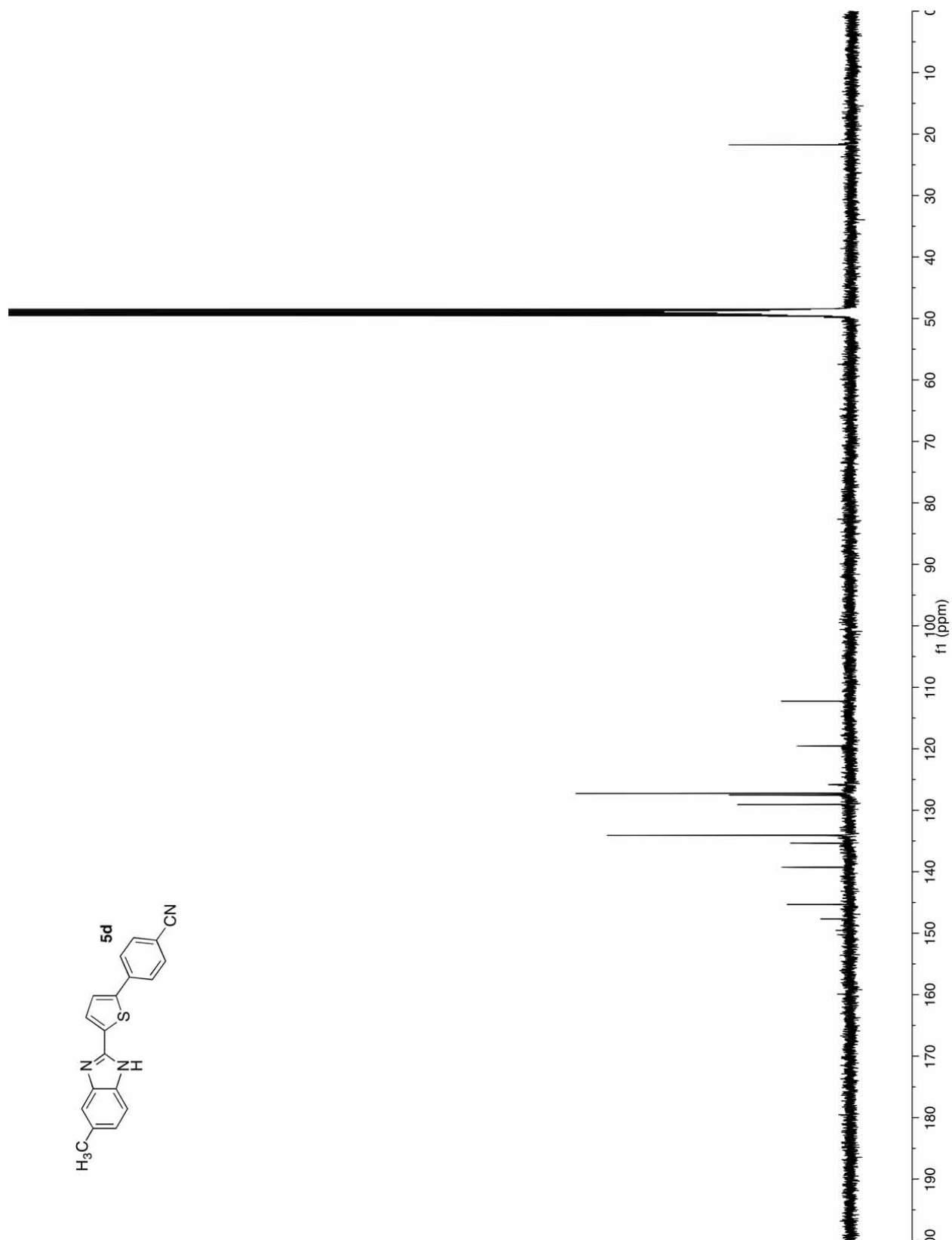
<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of 4-(5-(5-Methyl-1H-benzo[d]imidazol-2-yl)furan-3-yl)benzonitrile (**5c**).



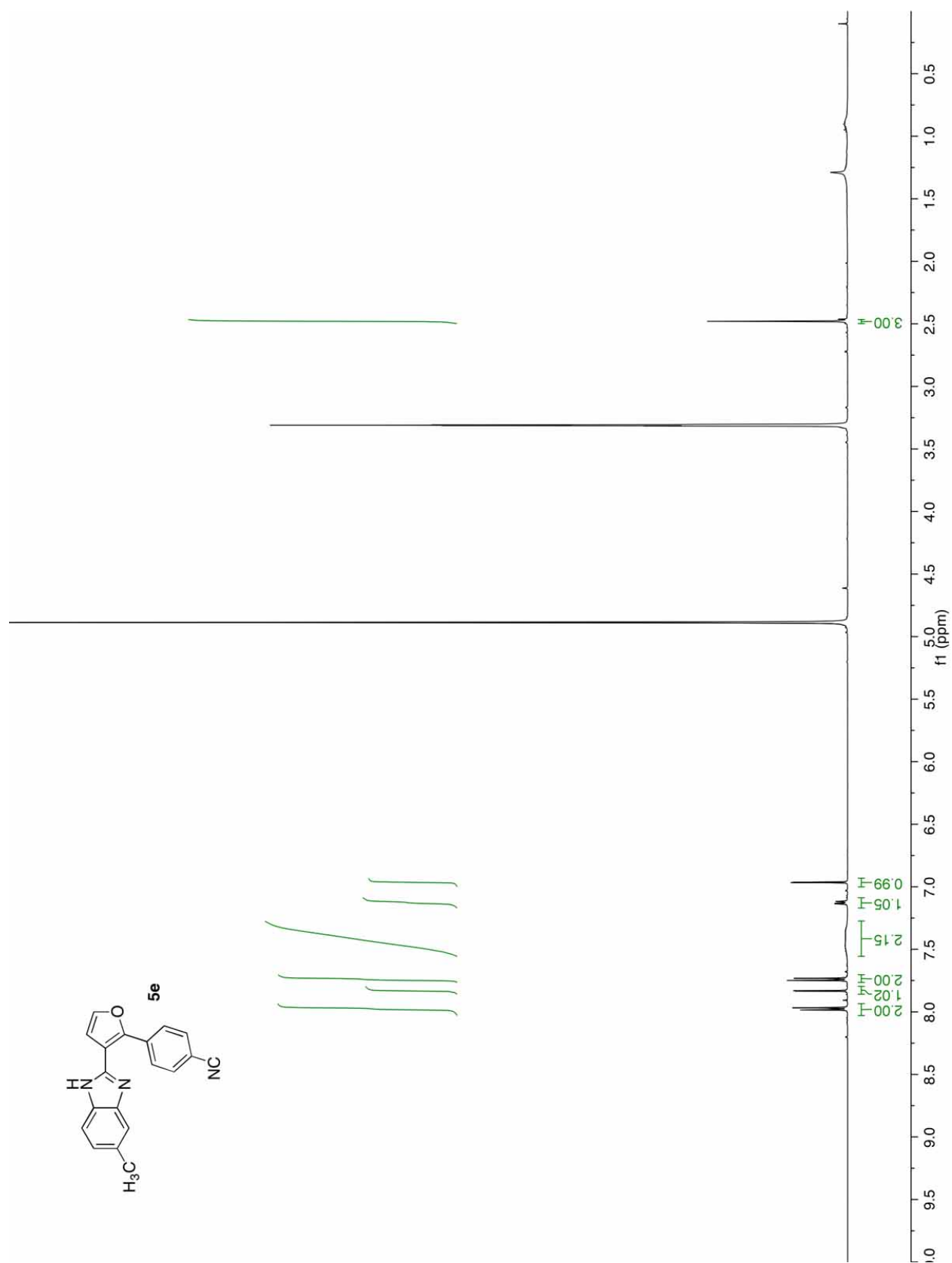
$^{13}\text{C}$  spectrum (125 MHz,  $\text{CDCl}_3$ ) of 4-(5-(5-Methyl-1H-benzo[d]imidazol-2-yl)furan-3-yl)benzonitrile (**5c**).



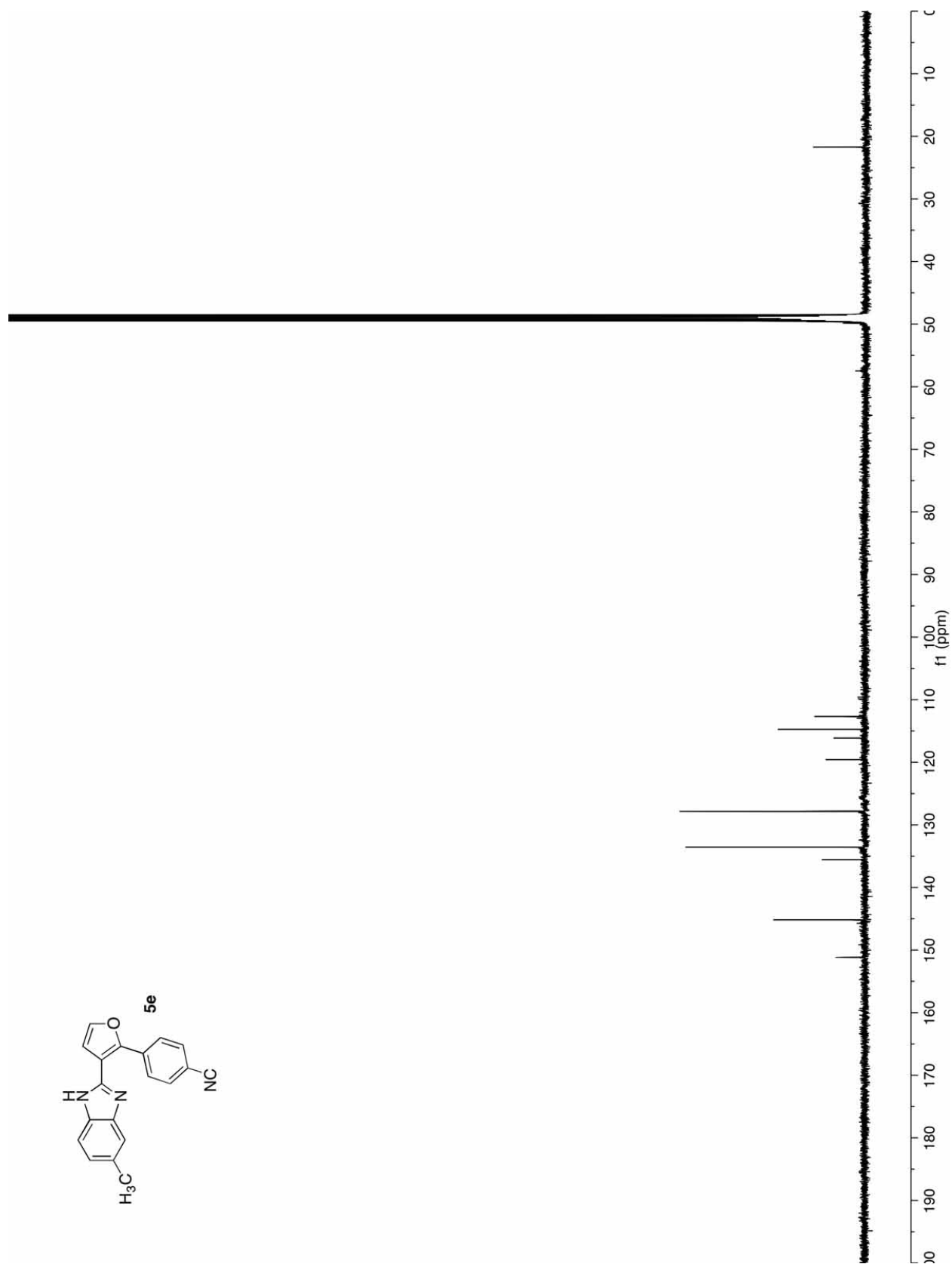
<sup>1</sup>H spectrum (500 MHz, CD<sub>3</sub>OD) of 4-(5-(5-Methyl-1*H*-benzo[*d*]imidazol-2-yl)thiophen-2-yl)benzonitrile (**5d**).



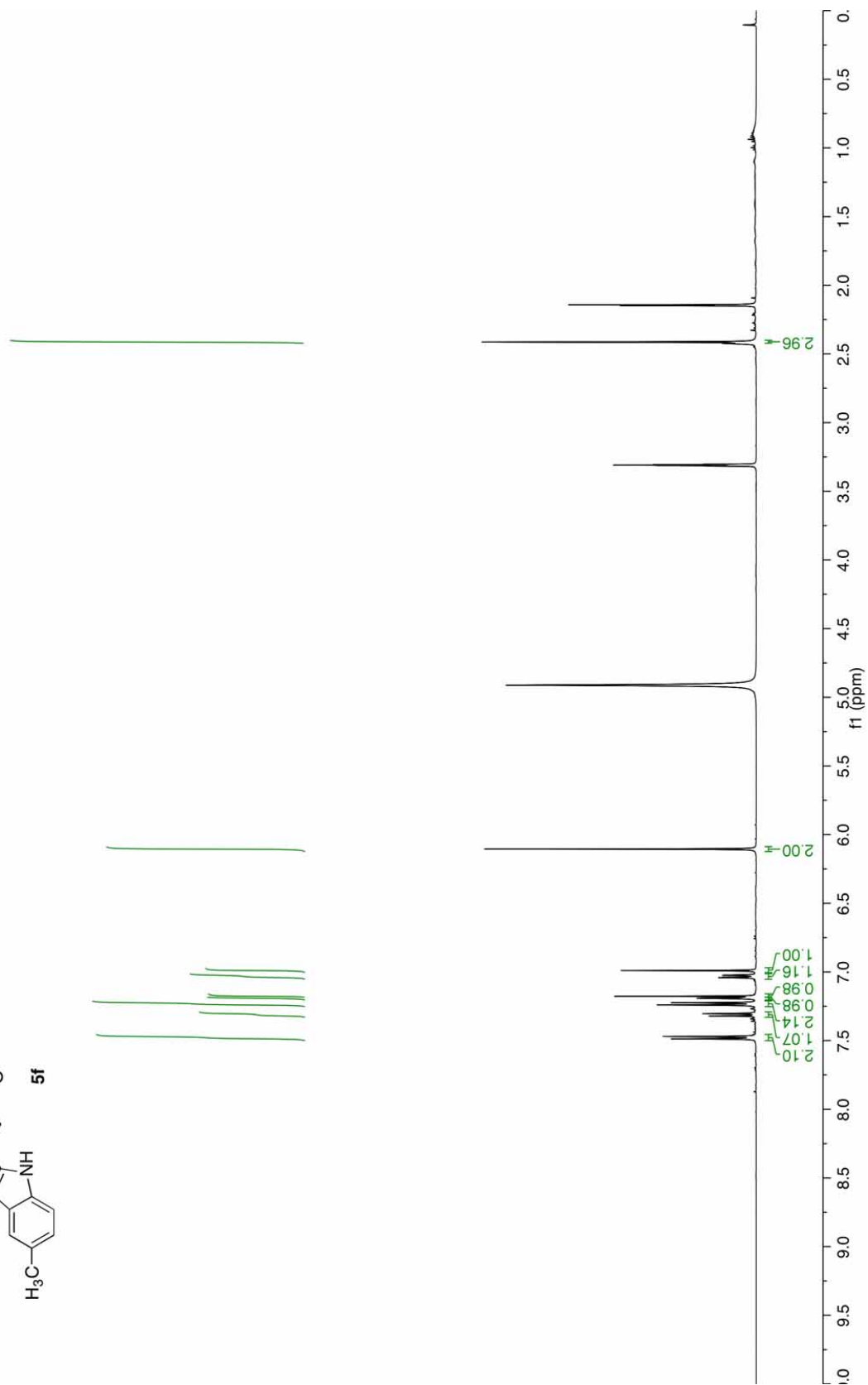
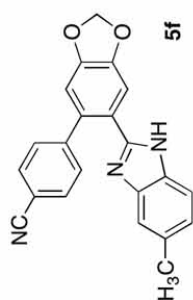
<sup>13</sup>C spectrum (125 MHz, CD<sub>3</sub>OD) of 4-(5-(5-Methyl-1*H*-benzo[*d*]imidazol-2-yl)thiophen-2-yl)benzonitrile (**5d**).



<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of 4-(3-(5-Methyl-1H-benzo[d]imidazol-2-yl)furan-2-yl)benzonitrile (**5e**).



<sup>13</sup>C spectrum (125 MHz, CDCl<sub>3</sub>) of 4-(3-(5-Methyl-1*H*-benzo[*d*]imidazol-2-yl)furan-2-yl)benzonitrile (**5e**).



<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of 4-(6-(5-Methyl-1*H*-benzo[*d*]imidazol-2-yl)benzo[*d*][1,3]dioxol-5-yl)benzonitrile (**5f**).

